# DURABILITY ASPECTS OF FLY ASH AND SLAG IN CONCRETE

## WORKSHOP PROCEEDING

FROM A

## NORDIC MINISEMINAR

OSLO - NORWAY

15. – 16. FEBRUARY 2012

# PREFACE

This publication contains 16 papers presented at a Workshop (Nordic Mini Seminar) concerning use of Type II additions as fly ash and slag in concrete.

The workshop was organised by Bård Pedersen and Claus K. Larsen from Norwegian Public Roads Administration & Dirch H. Bager, DHB-Consult.

In order to stimulate discussions between the participants, the Workshop was arranged as a two-day residential course, located in Oslo, February 15. – 16. 2012.

Nordic Mini Seminars are workshops arranged solely for researchers from the Nordic Countries in order to strengthen the inter-Nordic co-operation. A few foreign specialists can however be invited. To further stimulate discussions, only participants actively contributing are invited. 75 such Mini Seminars have been held since 1975.

38 researchers from Denmark, Finland, Iceland, Norway, Sweden, Canada, the Netherlands Germany and the UK participated in the workshop.

The present publication is Number 10 in a special series of Workshop-Proceedings of the Nordic Concrete Research.

Nordic Concrete Research (NCR) is a bi-annual publication of The Nordic Concrete Federation, presenting research and practical experience in the field of concrete technology, both from structural and material perspective. Every third year one of the publications is devoted to abstracts from the Nordic Concrete Research Symposia. (Nordic Concrete Research – Research Projects 20XX). The next Concrete Research Symposium will be held in Reykjavik 19. to 21. of June 2013.

Papers published in NCR are normally thoroughly reviewed by three reviewers. The papers in the present proceeding have however not been reviewed in this way. Instead the authors revised their papers after the workshop, based on comments and information obtained there. The individual presentations can be found on the Norwegian public road Administration's homepage http://www.vegvesen.no/Fag/Publikasjoner/Publikasjoner as Report No. 149

Oslo, August 2012

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# CONTENTS:

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# Long-term practice experience with the use of blast furnace slag cement for concrete structures at Rijkswaterstaat

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## ABSTRACT

Long-term durability of infrastructure facilities is considered of prime importance in view of the large economic impact of premature maintenance. Consequently, a major objective of Rijkswaterstaat is to promote the design and execution of structures having a maintenance free operational service life. To this end the design specifications make the use of either blast furnace slag or fly ash cement obligatory. The long-term experience with these cements in reinforced concrete structures exposed to marine and de-icing salt environments has demonstrated that these blended cements have to be considered superior regarding resistance against chloride ingress and deleterious alkali-silica reaction.

**Key words:** infrastructure, chloride, slag, fly ash, freeze-thaw.

## 1. INTRODUCTION

### 1.1 General

For Rijkswaterstaat long-term durability of infrastructure facilities is considered of prime importance in view of the large economic impact of premature maintenance. Consequently, a major objective of Rijkswaterstaat is to promote the design and execution of structures having a maintenance free operational service life.

For both reinforced and prestressed concrete structures Rijkswaterstaat specifies a standard design service life of 100 years. In addition a number of restrictions to the European and national codes have been implemented in a Rijkswaterstaat guideline [1]. In this guideline the use of either blast furnace slag cement with a slag content in excess of 50% or cement containing more than 25% of fly ash is made obligatory.

The major advantages of blast furnace slag cement include the very low permeability with respect to chloride ingress, the low risk of deleterious alkali-aggregate reaction, the high sulfate resistance, the low heat of hydration, and the lower environmental impact ($CO_2$). However, concrete made with blast furnace slag is known to be more sensitive to curing conditions and scaling resulting from the combined action of frost-thaw and de-icing salts. On the other hand with proper curing these disadvantages can easily be overcome. In view of the relative mild exposure conditions during winter periods the resistance against freeze-thaw is considered of less importance for Dutch practice.

Nowadays in The Netherlands 3 production plants exist which are producing about 2.5 million tons per year of blast furnace slag. At present blast furnace slag cement has a market share of about 55%.

Most commonly blast furnace slag cement is preferred for cast-in-place concrete structures, whereas fly ash cement is generally favoured for prefabricated concrete elements.

### 1.2 Blue colour

During the first few days of exposure to air after demoulding surfaces of concrete made with blast furnace slag cement show a characteristic blue or even black appearance. This blue colouring results from the formation of iron and manganese sulphide during hydration. Upon exposure to air the blue appearance will gradually vanish as these sulphides will oxidize to iron and manganese sulphate. Well-cured concrete will demonstrate this blue colour longer than poor-cured concrete. In general, the slower the transition front of blue to grey penetrates into the concrete, the lower the permeability of the concrete cover zone. Therefore, the concrete colour can be considered an easy visual indicator of the achieved concrete quality. For good quality concrete the core portion of a structure may maintain its blue colour during several decades. Where it is observed in practice that the reinforcement steel is still embedded in blue concrete, corrosion will be absent as oxygen has not yet reached the level of the reinforcing steel [2]. Thus, the more blue and the longer this colour persists, the less reason for concerns on durability there should be.

### 1.3 General considerations

Reinforcement corrosion induced by the ingress of chloride ions from the exposure environment is considered a major threat to the long-term durability. However, Dutch practice has clearly demonstrated that chloride-induced corrosion in structures made with blast furnace slag cement concrete is rather scarce. In the incidences that damage due to reinforcement corrosion is observed this generally occurs in specific areas (mostly always near leaking joints) and where concrete cover thickness is shallow and cover quality is poor due to execution errors.

In The Netherlands for over more than 75 years, marine structures have been built exclusively with blast furnace slag cement. The most prominent project in which blast furnace slag cement has been used, was the Eastern Scheldt storm surge barrier with a design service life of 200 years. Investigations on chloride ingress in marine structures built along the North Sea indicate that transport of chlorides is very slow [3] and it is anticipated that the original design service life will be achieved without major maintenance being necessary.

For bridges and viaducts the use of blast furnace slag cement is advocated by Rijkswaterstaat in view of the risk of deleterious alkali-silica reaction. Generally, carbonation is not considered a serious problem provided adequate cover depth has been achieved, complying with the requirements according to the prevailing codes.

# 2. EXAMPLES OF CONCRETE STRUCTURES MADE WITH BLAST FURNACE SLAG CEMENT

## 2.1 Noordersluis IJmuiden

The first project in The Netherlands in which blast furnace slag cement (imported from Germany) was used on a large scale dates from 1919 (North Sea Canal locks near IJmuiden; 1919-1930). An extensive test program clearly demonstrated the better performance of blast furnace slag cement in a seawater environment in comparison to the traditionally used Portland cement [2]. After more than 80 years of service in a marine environment, no signs of serious damage, either due to reinforment corrosion or chemical attack, have been detected, see Figure 1. In contrast, the discharge sluices and locks in the Afsluitdijk, a 32 km dike damming the former Zuiderzee from the North Sea, constructed in 1927-1930 using ordinary Portland cement, demontstrate serious deterioration from both sulphate attack and alkali-silica reaction.

*Figure 1 – Lock walls of the Noordersluis at IJmuiden during construction (1921-1929) and after 80 years of service.*

## 2.2 Haringvliet dam

As a result of the 1953 flooding disaster in the south-western part of the Netherlands, the so-called Delta project was developed aiming at strengthening the flood defences and cutting the coastline by 700 kilometres. This project comprised several major storm surge barriers, e.g. the Haringvliet dam, the Eastern Scheldt storm surge barrier and the Maeslant surge barrier, see Figure 2.

The Haringvliet dam was built between 1958 and 1970, with the piers being constructed during the time period 1961-1963 using a special blast furnace slag cement. This so-called Delta cement had a coarser grain size than usual as to mitigate heat generation during hydration. The slag content of the cement used was estimated to be between 50% and 65%.

In 2002 investigations were conducted as to obtain data on chloride ingress resulting from 40 years of exposure to a marine environment. In Figure 3 some typical examples of chloride profiles are shown which are obtained in the splash zone (just above the tidal zone) from the piers of the discharge sluices.

*Figure 2 – Discharge sluices in the Haringvliet dam and Eastern Scheldt storm surge barrier.*

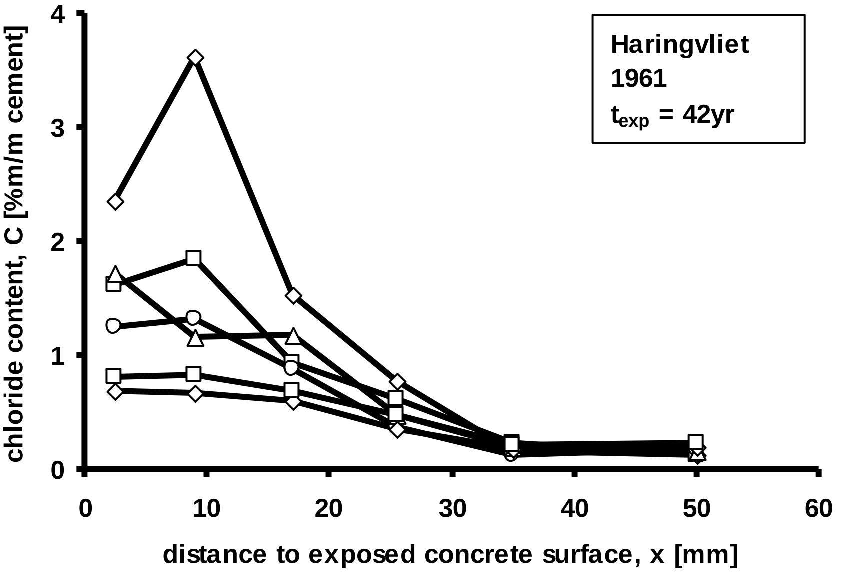

*Figure 3 – Measured chloride profiles in concrete cores retrieved from the piers of the Haringvliet dam after 42 years of exposure to a marine environment.*

Thereupon these chloride profiles were translated into quantified model parameters by regression analysis using the mathematical solution to Fick's 2nd law of diffusion, see Figure 4. Based on these measurement results the time to corrosion initiation is anticipated to vary between 216 and 405 yr (c = 70mm; $C_{crit}$ = 0.4%), discarding any decrease of the apparent diffusion coefficient, $D_a$, over time, i.e. assuming the ageing factor n = 0. This is considered to be a conservative estimate as the ageing factor for concrete made with blast furnace slag cement is considered to amount to 0.45 [4] or to 0.50 [5]. However, it may be justified to use n = 0 for concrete structures having an age in excess of 40 years. Consequently, during the forthcoming decades no major maintenance activities are foreseen to take place.

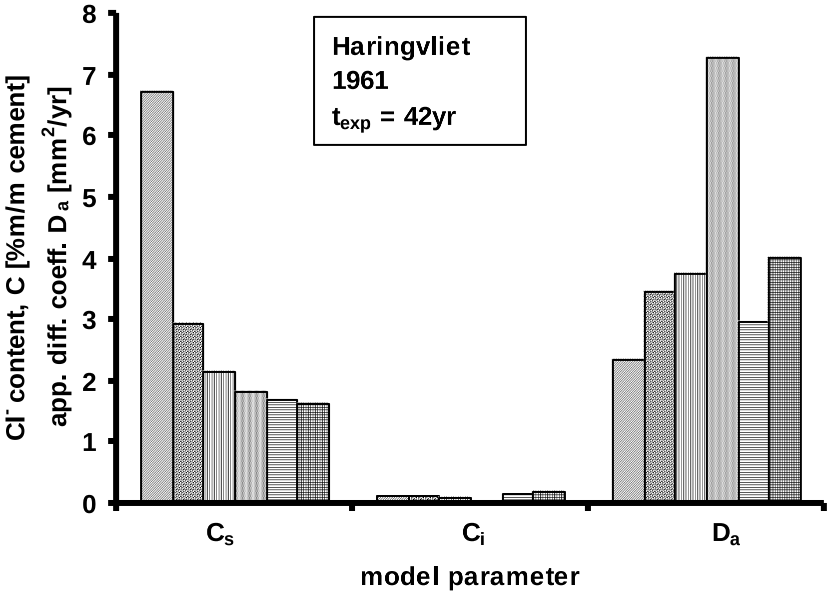

*Figure 4 – Quantification of model parameters $C_s$, $C_i$ and $D_a$ based on regression analysis of measured chloride profiles for piers in the Haringvliet dam.*

## 2.3 Alkali silica reaction

Damage resulting from deleterious alkali silica reaction was considered uncommon in the Netherlands until 1995 when ASR was detected in a number of viaducts built in the 1960's using Portland cement concrete. In view of widely spread occurrence of delamination in the deck and the associated risk of structural failure most of these structures have been demolished within a few years after detection of ASR. The viaduct shown in Figure 5 was demolished in half a day, without any concrete chunks adhering to the reinforcing steel. Based on the findings that ASR was found in concrete made with ordinary Portland cement only, as a preventive measure Rijkswaterstaat has made the use of cement containing at least 50% of slag or 25% of fly ash obligatory [1].

*Figure 5 – Demolished concrete viaduct which suffered from deleterious ASR.*

## 2.4 Freeze-thaw

Damage resulting from frost-thaw is hardly observed in the Netherlands, however scaling of the concrete surface due to the combined action of frost-thaw and exposure to de-icing salts is frequently observed. Initially, blast furnace slag cement concrete appears to scale faster but after some time the scaling rate becomes less compared to Portland cement concrete [2]. In Dutch practice concrete with a water to cement ratio less than 0.45 is considered to be resistant against the combined action of freeze-thaw and de-icing salt, regardless of the type of cement. For road structures Portland cement concrete or Portland fly ash cement is commonly used to prevent the occurrence of surface scaling at an early age. It should be noted that in contrast to most other European countries air entrainment is commonly not prescribed in the Netherlands.
During the relatively severe winter periods of 2009 to 2011 an increased number of incidences has been reported on early age scaling, predominantly for concrete components made with blast furnace slag. Although there is no clear evidence, there is a strong belief that this damage has resulted from inadequate curing procedures by the contractor. In [6] these incidences have been evaluated and it was concluded that adequate resistance against freeze-thaw attack with or without exposure de-icing salt can only be achieved through air entrainment, for all types of cement.

## 3. DEVELOPMENTS ON PERFORMANCE-BASED SPECIFICATIONS

At Rijkswaterstaat it is implicitly agreed upon that the European codes give acceptable cover depths provided concrete is made with blast furnace slag and fly ash cement. In view of the significant advantages the Rijkswaterstaat Guideline [1] therefore requires a minimum slag content of 50% for ready-mix concrete, whereas for prefabricated concrete elements either a minimum content of 50% slag or 25% of fly ash is required.

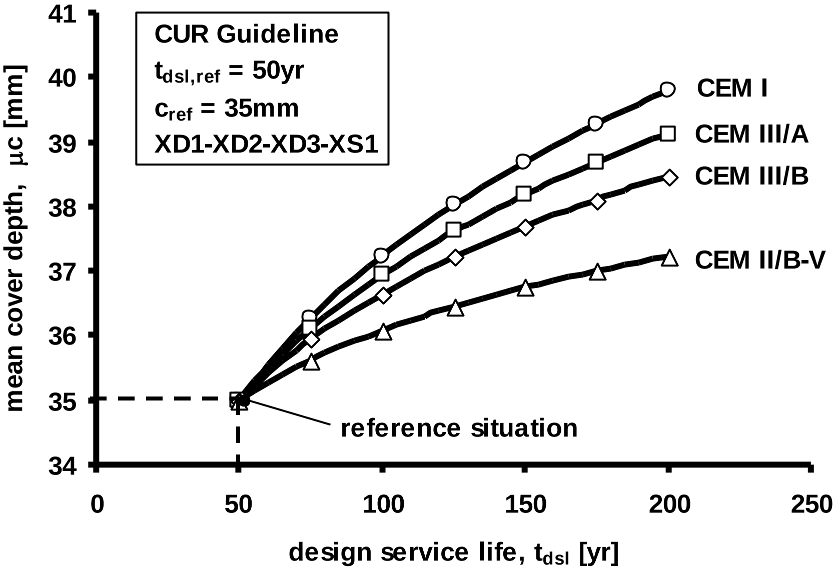

*Figure 6 – Relationship between design service life and thickness of concrete cover according to the calculation procedure adopted in [5]; reference situation: $t_{dsl}$ = 50yr; $\mu c$ = 35mm.*

In practice, particularly in the precast concrete industry, a need has been expressed for a performance-based approach as to allow cover depths less than those required by the codes. In 2009 a first attempt was made through a CUR Guideline [5], however the approach adopted appeared to be incorrect, unrealistic and unpractical [7]. As an example, the unrealistic nature of the semi-probabilistic approach can be demonstrated by the resulting relationship between design service life and cover depth, as shown in Figure 6. According to [5] for most concrete qualities an increase of less than 5mm would extend the design service life from 50 years to 200 years. Moreover, ready-mix concrete producers encountered serious problems as previously accepted concrete mixes gave essentially non-reproducible levels of the chloride migration coefficient, $D_{nssm}$, in the course of time. At present Rijkswaterstaat has taken the initiative to develop it's own performance-based approach together with concrete industry. In view of past experience this approach will only rely on the use of blast furnace slag and fly ash cement for infrastructure facilities.

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# ““The k-value concept”, the “Equivalent Performance of Combinations Concept” and the “Equivalent Concrete Performance Concept””

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## ABSTRACT

The paper gives a brief description on how secondary cementitious materials as fly ash, micro silica and slag can be used in concrete production.

**Key words:** The k-value concept, Equivalent Performance of Combinations Concept, Equivalent Concrete Performance Concept, secondary cementitious materials, Type II additions, EN206-1.

## 1. INTRODUCTION

Use of secondary cementitious materials as partial replacement for cement in concrete has been used for many years. In particular, additions with pozzolanic properties as fly ash (FA) and micro silica (MS) have been taken into account in the European Concrete standard EN 206-1 as type II additions.

In EN 206-1 use of Type II additions as FA and MS are being dealt with using the k-value concept. However, in some countries as United Kingdom, the Netherlands and Portugal, another approach, the “Equivalent Performance of Combinations Concept - EPCC” has been used – more or less identical in the three countries..

Currently, in EN 206-1, some rough rules for national acceptance of new cement types and binder combinations are laid down in annex E. An attempt to have principles for this more generally defined are ongoing; the “Equivalent Concrete Performance Concept - ECPC”. (CEN TC 104 / SC1 / TG 17)

Ground Granulated Blast Furnace Slag (GGBFS) have been used for quite some years, mainly as a constituent in CEM II and CEM III types of cement, but also as an addition during concrete manufacture. Since the product standard EN 15167-1 was published in 2006, GGBFS shall be treated in the same manner as FA and MS in EN 206. During the last years, this has been a major item for discussion in CEN TC 104 / SC 1 / TG 5 “Use of Additions”, in order to prepare rules for use for GGBFS in EN 206.

## 2. THE “K-VALUE CONCEPT”

The k-value concept is a prescriptive concept which is based on the comparison of the performance (durability or strength as a proxy-criterion for durability where appropriate) of a reference concrete with cement "A" against a test concrete in which part of cement "A" is replaced by an addition as function of the water/cement ratio and the addition content.

The k-value concept permits type II additions to be taken into account:

- by replacing the term “water/cement ratio” with “water/(cement + k * addition) ratio”; and
- the amount of (cement + k * addition) shall not be less than the minimum cement content required for the relevant exposure class

In prEN 206:2011, the following rules for use for FA, MS and GGBFS are given: (prEN 206:2011 are under CEN enquiry during the spring and summer of 2012. The final accepted version of EN 206 is expected in the beginning of 2013.). Section 2.1 – 2.3 are extracts from prEN206:2011.

In EN 206-1 only CEM I types are taken into account. prEN 206 include also CEM II/A cements.

## 2.1 k-value for fly ash conforming to EN 450-1

a) A k-value of 0.4 is permitted for concrete containing cement types CEM I and CEM II/A conforming to EN 197-1.

b) For use with CEM I cement, the maximum amount of FA to be taken into account shall meet the requirement:

  - o FA/cement ≤ 0.33 by mass.

c) For use with CEM II/A cement, the maximum amount of FA to be taken into account shall meet the requirement:

  - o FA/cement ≤ 0.25 by mass.

d) If a greater amount of FA is used, the excess shall not be taken into account for the calculation of the water/(cement + k * FA) ratio and the minimum cement content.

## 2.2 k-value for micro silica of class 1 conforming to EN 13263-1

a) The following k-values are permitted to be applied for concrete containing cement types CEM I and CEM II/A (except CEM II/A-D) conforming to EN 197-1:

  - o for specified water/cement ratio ≤ 0.45 k = 2.0
  - o for specified water/cement ratio > 0.45 k = 2.0 except for exposure classes XC and XF, where k = 1.0.

b) The maximum amount of MS to be taken into account shall meet the requirement:

  - o MS/cement ≤ 0.11 by mass.

c) If a greater amount of MS is used, the excess shall not be taken into account for the calculation of the water/(cement + k * MS) ratio and the minimum cement content.

d) (4) The amount of cement shall not be reduced by more than 30 kg/m³ below the minimum cement content required for the relevant exposure class.

National provisions may apply for MS of class 2. (MS of class 2 have a content of $SiO_2$ above 80%, while MS of class 1 have $SiO_2$ content above 85%). In Denmark, regulations for the two classes are identical.

## 2.3 k-value for ground granulated blast furnace slag conforming to EN 15167-1

a) The k-value and the maximum amount of ground granulated blast furnace slag (GGBFS) to be taken into account for the k-value concept shall be in accordance with the provisions valid in the place of use.
b) A k-value of 0.6 for concrete containing cement types CEM I and CEM II/A conforming to EN 197-1 is recommended for any GGBFS conforming to EN 15167-1. The maximum amount of GGBFS should meet the requirement:
    - GGBFS/cement ≤ 1.0 by mass.
c) If a greater amount of GGBFS is used, the excess shall not be taken into account for the calculation of the water/(cement + k * GGBFS) ratio and the minimum cement content.

The author does accept, and understand, the slag producer’s interest in having as high as possible k-value for GGBFS. However, we shall recognize that the k-value concept basically shall correlate the durability of concrete with known and accepted cement types (cement and generally accepted Type II additions) with concrete with other constituents as GGBFS.

The k-value of 0.6 for GGBFS recommended here is considered as a “safe” generic value. Thus tests according to the EPCC and ECPC concepts (see sections 3 and 4), might document higher values. In this way influence of combinations of cement and GGBFS of specific producers can be taken into account in countries where the EPCC and ECPC principles will be accepted and adopted, while other countries can use GGBFS in the same "safe" way, as currently for fly ash and micro silica.

In Denmark the EPCC and ECPC principles will not be applied within a long time scale. Thus, if a "safe" k-value for GGBFS, like for FA and MS, cannot be accepted for EN 206, then the use of GGBFS as a type II addition can hardly be expected to be accepted for use in Denmark. Until now, GGBFS has not been allowed for use in Denmark.

## 2.4 Current used k-values within the Nordic countries

Additions of type II have been used for many years within the Nordic countries. Table 1 gives the k-values used within the five countries.

*Table 1: Currently used k-values in the Nordic countries*

| Country | Product | k-value | Comments |
|---|---|---|---|
| Denmark | FA<br>(Category A) | 0.5 | CEM I, CEM II/A-L, CEM II/A-LL |
|  | MS<br>(Class I & II) | 2.0 | CEM I, CEM II/A-L, CEM II/A-LL, CEM II/A-V, CEM II/B-V. |
|  | GGBFS | - | Not accepted for use |
| Finland | FA | 0.4 | CEM I, CEM II/A-S, CEM II/A-D, CEM II/A-V, CEM II/A-LL, CEM II/A-M, CEM II/B-S, CEM II/B-V, CEM II/B-M, CEM III/A, CEM III/B. Additions included in the cement are taken into account as type II addition in the concrete |
|  | MS<br>(Class I & II) | 1.0/2.0 |  |
|  | GGBFS | 0.8<br>1.0 in XA |  |
| Iceland | FA | - | Not accepted for use |
|  | MS | 1.0 |  |
|  | GGBFS | - | Not accepted for use |
| Norway | FA | 0.2/0.4 | CEM I |
|  | MS | 1.0/2.0 | CEM I, CEM II/A-S, CEM II/B-S, CEM II/A-D, CEM II/A-V, CEM II/B-V and CEM III/A dependent on exposure class |
|  | GGBFS | 0.6 | CEM I, CEM II/A-L, CEM II/A-S, CEM II/B-S, CEM II/A-D, CEM II/A-V, CEM II/B-V and CEM III/A |
| Sweden | FA | 0.4 | CEM I and CEM II |
|  | MS<br>(Class I & II) | 1.0/2.0 |  |
|  | GGBFS | 0.6 |  |

### 2.5 Some thoughts on the k-value

In the author’s point of view, calculation of k-values for type II additions alone based on their influence on the 28 days compressive strength has no real meaning. If this should be a criteria, the k-factors for fly-ash and micro silica should be app. 0.3 and >3 respectively.

The k-value concept was introduced as a kind of quality criteria for type II additions, even before "Type II" was defined in EN 206. In Denmark we decided on k-values of 0.5 for fly-ash and 2 for micro silica in 1987! These values was based on examination on "equivalent" types of concrete with CEM I and CEM I + additions. Measurements/judgements were made on mechanical properties, chloride intrusion, freeze/thaw durability, thin sections analysis etc. on concrete samples exposed in real structures for some/several years, as well as on laboratory investigations. To our judgements, the factors of 0.5 & 2 respectively seemed to be reliable. Later, within CEN, factors of 0.4 and 2 were accepted. Hence, we feel, that our values did represent a good European consensus, and that our approach has been reasonable. (Of course, this approach was rather easy in a country as Denmark, with only one cement producer, a few power plants and import of two types of micro silica.)

Later, use of GGBFS have been studied several times in Denmark – The author have been researcher in studies, involving a lot of different types of GGBFS, with regard to producers, fineness, colour (grey & white) and combinations with Danish cement types. In these studies -

based on investigations comparable with the ones used formerly for judgement of k-values for Fly ash and Micro silica, although mainly based on laboratory measurements, a GGBFS which could be recommended for a k-value higher than 0.6 have never been tested {This is mainly based on tests with cements of strength class 52.5 MPa}

Today, huge efforts are made by the cement industries and concrete producers to reduce the $CO_2$ impact on the environment. However, such environmentally efforts shall be made with due reference to the final product, i.e. durability aspects. Proper use of type II additions, both within the cement manufacture and in the concrete industry, can certainly reduce the $CO_2$ impact. However, if the concept for using such materials is not scientific valid for long time durability of concrete, it is difficult to believe, that for example an estimated 120 years life time for a submerged tunnel, will be based on a 28 days compressive strength measurement on a mixture of CEM Y cement + Z% type IIX addition.

## 3 EQUIVALENT PERFORMANCE OF COMBINATIONS CONCEPT

The 'Equivalent Performance of Combinations Concept' treats a combination of cement and an addition (or additions) as being technically equivalent to a standardized cement of the same nominal composition. This concept may permit a defined range of combinations to count fully towards the requirements for maximum water/cement ratio and minimum cement content, which are specified for the standardized cement.

When applying this concept, it is recommended to:

- Identify a cement type, which complies with a European cement standard, which has the same (or very similar) composition to the intended combination.

- Assess whether the combination can be assumed to have adequate strength as well as the relevant physical and chemical properties, which the cement standard requires for the identified cement type. Note that: In the case where the specification for the concrete includes a minimum requirement for strength, it can be assumed that if the concrete meets this strength requirement, then the combination has adequate strength; otherwise, a suitable testing programme should be established.

- The physical/chemical requirements in the addition product standard will generally ensure that the combination has equivalent physical and chemical properties to the cement type and further testing will not normally be necessary.

- However, if there is concern that the combination may not satisfy any essential physical or chemical property or if special properties (e. g. heat of hydration or pozzolanicity) are required, a suitable testing programme should be established.

- Any necessary testing should be carried out at least monthly using representative samples of the cement and addition(s) that are being combined.

## 4 EQUIVALENT CONCRETE PERFORMANCE CONCEPT

- The “Equivalent Concrete Performance Concept” permits amendments to the requirements for minimum cement content and maximum water/cement ratio when one or more specific additions and one or more specific cements are used, for which the manufacturing source and characteristics of each are clearly defined and documented.

- It shall be proven that the concrete has an equivalent performance especially with respect to its reaction to environmental actions when compared with a reference concrete in conformity with the requirements for the relevant exposure class

- The concept shall be used only for cements conforming to EN 197-1 with type II additions fulfilling requirements in EN product standards.

Provisions valid in the place of use may place restrictions on the cement types and fly ash loss-on-ignition categories to align the composition to currently permitted cements and they may extend this rule of application to other additions conforming to provisions valid in the place of use, e. g. other fly ashes.

More detailed information regarding EPCC & ECPC will be available in CEN Technical reports.

It is expected that the EPCC will be adopted in the revised version of EN 206 in 2013, while the ECPC concept is too premature. Use of the EPCC concept will be decided by the national member bodies; hence the concept will not be adopted and applied in all countries.

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|---|---|
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| prEN 206:2011 | “Concrete – specification, performance, production and conformity”<br>CEN TC 104 / SC 1 N 719 |
| EN 450-1 | Fly ash for concrete - Part 1: Definition, specifications and conformity criteria |
| EN 13263-1 | Silica fume for concrete - Part 1: Definitions, requirements and conformity criteria |
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# ISO 16204, Durability – Service Life Design of Concrete Structures

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## ABSTRACT

The provisions to ensure a specified service life of a concrete structure given in most operational standards are prescriptive in nature. Normally the justifications of the requirements are not transparent to the reader. This paper describes an initiative from fib and ISO to establish a methodology for handling these matters in a more analytical and transparent way when designing new structures or when assessing an existing structure's remaining service life.
The methodology is based on a probability based limit state approach in the same manner as normally applied in structural design. It is supposed that ISO 16204 will be published in 2012.

**Key words:** Service life design, concrete, limit state, probabilistic, durability.

## 1. INTRODUCTION

The durability of structures, and thus the expected length of their service life, is a major parameter when considering the economical and environmental impact of design and construction. Today most operational concrete standards worldwide are based on deemed-to-satisfy requirements concerning the durability of these structures. These requirements are normally linked to proxy criteria like maximum w/c ratio, cement type, cover to the reinforcement and crack limitations.
The limiting values given in the standards are based on the expert opinion of the code committee.
There are several weaknesses by this traditional approach:

- It is often unclear which condition represents the end of the service life.
- The required level of reliability for the design is often unclear.
- The criteria should be based on long-term field experience. Such experience is however normally not available for modern materials and design concepts, and concepts with longer service record than 50 years are seldom in use any more. Predictions and extrapolations by modelling are therefore needed.

Some 10 years ago a group of engineers made an initiative to establish a methodology on service life design of concrete structure that could improve the situation. This initiative has since matured under the auspices of fib, and later in the environment of ISO. ISO 16204 "Durability –

Service life design of concrete structures" is presently for formal vote and is expected to be launched coming autumn.

## 2. BACKGROUND

Durability of concrete structures, and in particular the lack of such, has been in the focus of the general society the last few decades. Excessive repair-needs have challenged our industry.

In 1998, a group of 19 European enthusiasts signed a contract with the European Commission to develop a platform for durability design of concrete structures that contained the same elements and philosophy as that of modern structural design. At "DuraNet"'s final workshop in Tromsø, Norway in 2001, attendees from Europe and North America worked out a plan for how to progress to get this methodology standardized and implemented in the industry worldwide. The obvious environment for this was ISO. Some of us therefore met at the ISO TC-71 meeting in Oslo that autumn and presented our visions. TC-71, being responsible for concrete related standardization within ISO, endorsed the initiative, but correctly made us aware of that ISO normally starts their work on the basis of existing documents. We therefore agreed to ask the international concrete federation, fib, to work out such a model for a standard.

fib then formed Task Group 5.6 under the chairmanship of Peter Schiessl and with experts from Europe, North and South America and Japan.

The group early decided to make a document in full parallel to ISO 2394 "General principles on reliability for structures". This standard forms the reference for most modern standards for structural design. ISO 2394 is also the "mother document" for the European Eurocode-0 "Basis of structural design" (EN 1990). fib then based its approach on a limit state (LS) and reliability based concept. In 2006, fib Model Code for Service Life Design (MC SLD, bulletin no 34) was endorsed by fib's General Assembly in Naples, Italy. These provisions are later implemented in the new general Model Code endorsed by fib last autumn.

## 3. END OF SERVICE LIFE

The limit-state concept recognizes the need to be specific about what represents the "end of service life".

The application of reliability based and limit state based service life design is by both ISO 2394 and EN 1990 specifically excluded from the scope of these documents. The task for TG 5.6 was then to come up with the needed amendments to these reference documents.

By the first glimpse, these ideas might be considered as revolutionary, but actually that is not true.

All standard writers during the past must have had some idea of what they considered the "end of service life" when they did come up with their provisions. They must have had an idea if they considered rust stains or full structural collapse. They then applied a "limit state" concept. They must also have had in mind if they expected the average of the building population to stand this service life length, or if they expected the great majority of the population to stand this requirement. They then applied a probabilistic approach.

However, it is fair to state that these processes were very seldom applied in a transparent way.

This lack of precision is easily found in for instance European standards. In Europe we have implemented the EN-206 /EN 13670 / EN 1992 in 31 countries. Durability is however still regarded as under national authority. Requirements like “maximum w/c ratio” and “minimum cover to the reinforcement” are therefore given in the national annexes to these standards.

The spread of requirements for structures expected to be subject to similar conditions is striking. Examples are for Environmental classes XC3 (exposed to carbonation – sheltered from rain), XC4 (exposed to carbonation – exposed to rain) and XS2 (submerged in sea water) for 50 years design service lives are:

| | | |
|---|---|---|
| Range of XC3 provisions for CEM I in Europe | UK → w/c < 0.55 and<br>25 mm minimum cover | DE → w/c < 0.65 and<br>20 mm minimum cover |
| Range of XC4 provisions for CEM I in Europe | NL → w/c < 0.50 and<br>25 mm minimum cover | DE → w/c < 0.60 and<br>25 mm minimum cover |
| Range of XS2 provisions for CEM I in Europe | UK → w/c < 0.50 and<br>35 mm minimum cover | NO → w/c < 0.40 and<br>40 mm minimum cover |

The differences in performance for these extremes are very large.

Having in mind that the technical expertise on these matters are more or less at the same level in these countries, the explanation must be that the different national standardisation bodies had different understanding of what actually represents the end of service life as well as the intended level of reliability.

Discussions in the present fib TG 5.11 has also revealed that the reliability index β applied in the discussions in some of the European national standardization bodies have varied from 1.8 (NL) to 0 (ES) (acceptance for failure, pf ranges from 4 % to 50 %) for the Limit State of depassivation.

The limit-state concept recognizes the need to be specific about what represents the “end of service life”. A main element in fib MC SLD, and the coming ISO 16204, is therefore an amended quantitatively definition to the qualitative one you will find in traditional standards like for instance in ISO 2394 or EN 1990:

| | |
|---|---|
| The traditional qualitative definition: | *The design service life is the assumed period for which a structure or part of it is to be used for its intended purpose with anticipated maintenance but without major repair being necessary.* |
| The quantitative amendment by fib and ISO: | *The design service life is defined by:*<br>• *A definition of the relevant limit state*<br>• *A number of years*<br>• *A level of reliability for not passing the limit state during this period* |

In principle the LS may be any condition that makes the building owner feeling uncomfortable. For concrete structures corrosion of the reinforcement is often the critical deterioration process. The LS could then be depassivation, cracking, spalling or collapse (ultimate LS). Due to the problem of developing reliable time-dependent models for the rate of corrosion (after depassivation), “LS-depassivation” is the choice of convenience for most engineers.

## 4. LEVEL OF RELIABILITY – CONSEQUENCES OF FAILURE

ISO 2394 suggests a 3 level differentiation of the consequences by passing a LS.

a) *risk to life low, economic, social and environmental consequences small or negligible*
b) *risk to life medium, economic, social and environmental consequences considerable*
c) *risk to life high, economic, social and environmental consequences very great*

Based on the relevant consequence class, combined with a consideration of the cost of safety measures, a relevant level of reliability for not passing the LS during the design service life should be selected. fib MC SLD and ISO 16204 suggest, in line with ISO 2394, $p_f = 10^{-1}$ for depassivation of reinforcement (by carbonation or chlorides) in the cases when the access of oxygen and moisture makes corrosion possible. If collapse is the considered LS, $p_f = 10^{-4}$ to $10^{-6}$ may be the relevant level if the possible consequences are in consequence class c).
Within the limitations normally found in the national building legislation, the LS and the related reliability level used in the design shall be agreed with the owner of the structure.

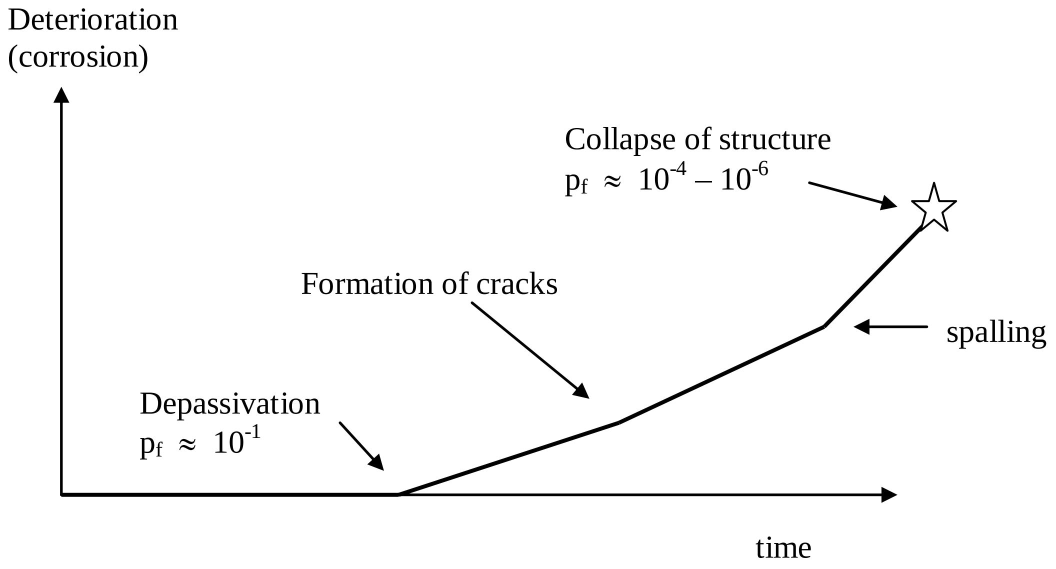

*Figure 1 - Example for corrosion of reinforcement. Various Limit States and corresponding levels of reliability.*

## 5. METHODS FOR VERIFICATION OF THE DESIGN

It shall be verified that the chosen design for a structure (location, lay-out, geometry, materials selection etc) will stand the design criteria given according to the definition of design service life.
fib MC SLD and ISO 16204 give 4 different ways of doing such verification:

| | |
|---|---|
| The full-probabilistic method: | The time to reach the LS with the required level of reliability is calculated based on statistical data for the environmental load and structural resistance. |

| | |
|---|---|
| The partial-factor method: | As for the full-probabilistic method, but the statistical data for load and resistance are substituted by characteristic values and partial coefficients |
| The deemed-to-satisfy method: | A set of requirements (normally w/c, cover to the reinforcement, crack width, air entrainment etc) that are prequalified by the code committee to stand the design criteria. |
| The avoidance-of-deterioration method: | This method implies that the deterioration process will not take place due to for instance: separation of load and structure by e.g. cladding or membrane, using non-reactive materials, suppressing the reaction with electrochemical methods etc |

The partial-factor method and the deemed-to-satisfy methods both need to be calibrated, either by the full-probabilistic method, or on the basis of long term experience of building tradition.

Of these 4 options, the full-probabilistic method is obviously the most complicated and sophisticated. By this reason many academics have regarded it as the most prestigious and precise one. This is fundamentally wrong. Due to the normal lack of good and representative data, and uncertainty in modelling, the full-probabilistic method will seldom be feasible for the design of new structures. However, it is well suited for assessments of existing structures.

Both fib and ISO therefore assume that the two last options will be applied for the design of the great majority of new structures also in the future, however, then hopefully calibrated according to the principles given in ISO 16204.

## 6. ISO 16204 “DURABILITY – SERVICE LIFE DESIGN OF CONCRETE STRUCTURES”

As soon as fib had finalized its bulletin no 34, we started up the work in ISO TC-71/ SC-3 to transform the model code into an operational international standard. The activity is going on in WG-4 with at present 27 appointed experts with me as the convenor.

Presently we are in the final phase as the official inquiry ended in February this year. The final version, ISO/FDIS, will be for formal vote this spring/summer.

The ISO committee fully realise that design of new structures according to the full-probabilistic and partial-factor method will in most cases not be feasible for the moment. We therefore transferred the authority to mobilize these options to the relevant national standardization body.

To get these 2 methods operational for design of new structures we have stated a firm condition in the scope (ISO/DIS 16204, clause 1):

> *This International Standard is intended for the use by national standardization bodies when establishing or validating their requirements for durability of concrete structures. The standard may also be applied:*
>
> - *for the assessment of remaining service life of existing structures; and*
> - *for the design of service life of new structures provided quantified parameters on levels of reliability and design parameters are given in a national annex to this International Standard;*

In annex E to ISO 16204 we have given guidance for the content of a national annex to the standard. Topics to be covered by such national annex may be one or more from the following list:

- *Deemed-to-satisfy requirements calibrated according to the requirements of this International standard*
- *Avoidance-of-deterioration requirements calibrated according to the requirements of this International standard*
- *How to select input data for the deterioration models when doing service life design on new structures according to the "full probabilistic" and the "partial factor" format.*
- *Partial factors to be used when doing service life design on new structures according to the "partial factor" format.*
- *Specific provisions for reliability management*
- *Required level of reliability for various limit states*
- *Specific provisions for quality management*

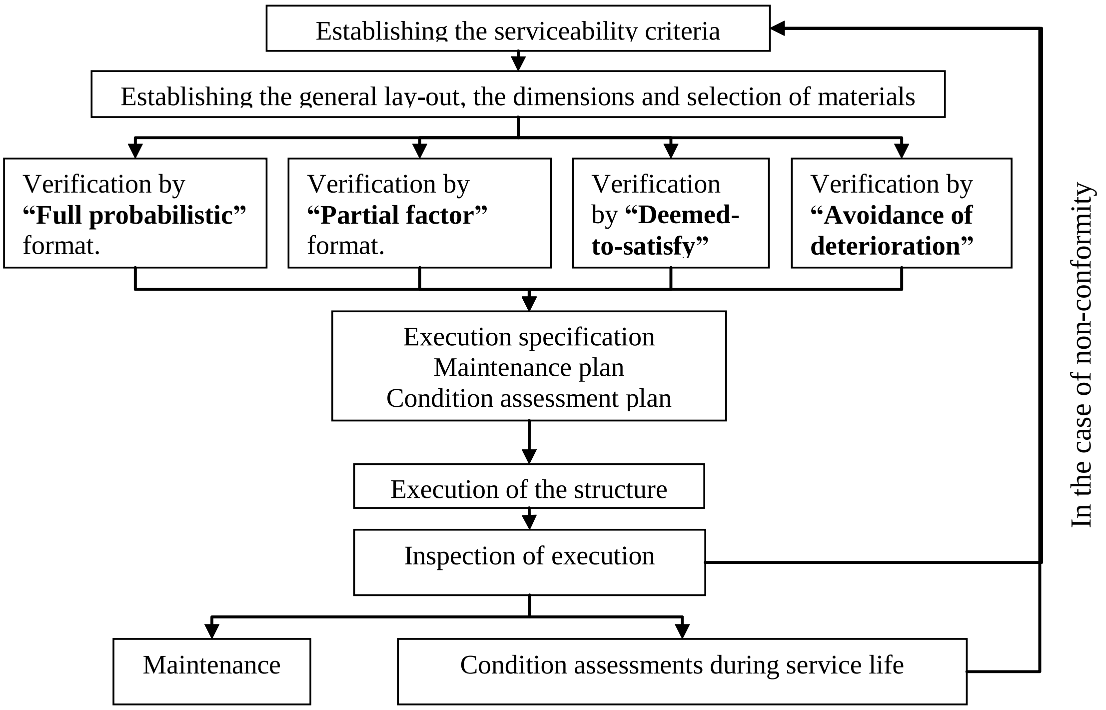

*Figure 2 – Flow-chart for service life design (from ISO/FDIS 16204)*

It is the hope of the authors of ISO 16204 that the principles and methodology of the standard will be implemented in future versions of EN 1992 / EN 13670 / EN 206 and thus make the durability provisions in these documents more consistent and transparent for the users.

Presently CEN has appointed a joint working group between CEN TC-250/SC2 (Eurocode-2) and TC-104 (EN 13670 and EN 206) to prepare the ground for the next major revision of these standards concerning the design of the service life.
The principles of fib Model code, as matured in ISO, are the backbone in these discussions.

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3. ISO/DIS 16204 “Durability – Service life design of concrete structures”
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5. EN 1992 “Design of concrete structures”
6. EN 13670 “Execution of concrete structures”
7. EN 206-1 “Concrete”

# Choice of binder in severe exposure classes – Swedish experiences and guidelines.

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## ABSTRACT

Swedish regulations for choice of concrete binder for civil engineering structures in severe exposure classes are presented and motivated. The requirements imply since many years the successful use of a CEM I cement with moderate heat, low alkali and sulphate resistance properties. Possible scenarios for development with slag or fly ash are reviewed.

**Key words:** Cement, concrete, durability, standards, regulations.

## 1. INTRODUCTION

### 1.1 Background

Swedish praxis for choice of binder in the most severe exposure classes, especially in salt-frost environment, called XF 4 in the concrete standard EN 206-1, has now for more than 25 years been influenced by the long perspective (120 years) durability thinking of the Swedish Road Administration (Vägverket, VV) nowadays the Swedish Transport Administration (Trafikverket, TRV)

Following a period during the 1970-ies with many observed salt-frost damages on bridges, even with air entrained concrete, Cementa conducted laboratory and field trials using a newly developed cement called Anläggningscement (short Anl, in English corresponding to cement for civil engineering structures). The cement is of type CEM I, supplemented with moderate heat (MH), low alkali (LA) and sulphate resistant (SR) properties.

In the middle of the 1980:ies VV prescribed the new type of cement to be used in bridge structures. There were many reasons for this decision.

As mentioned above many of the bridges built until then showed concrete damages, mainly caused by salt-frost deterioration.

A new method for testing salt-frost resistance on concrete had been developed by SP – Technical Research Institute of Sweden in the early 1980:ies, which made it possible for VV to require pretesting of the concrete mix design. The tests showed that concrete with Anl cement had very good resistance against salt-frost deterioration, even with moderate high air content.

Temperature cracking in massive civil engineering structures may lead to problems with water tightness and corrosion. Field tests showed that the temperature cracking susceptibility was lower for Anl than for other cements.

In some parts of Sweden a risk of slow alkali-silica reactive aggregates had been observed. Anl is a low-alkali cement and helped to control that risk.

The sulphate resistant property of the Anl cement was considered beneficial in some ground and tunnel structures.

### 1.2 Present situation

In terms of production Anl cement has grown substantially from a moderate start in the middle of the 1980:ies to more than 400 000 tonnes per year today. The demand exceeds the capacity at the Degerhamn factory and an Anl with similar composition and properties is produced at the Slite factory. Besides for the TRV structures the cement has been used at large infrastructure projects such as the Öresund bridge and the City tunnel in Malmö. The cement type is also one of the main alternatives for the Fehmarn Belt link.

## 2. STANDARDS AND REGULATIONS

The choice of binder in different exposure classes is regulated in the Swedish standard SS 13 70 03 Concrete – Application of EN 206-1 in Sweden.

The present edition of SS 13 70 03:2008 was prepared by a special ad-hoc group through a close examination of the state of knowledge concerning durability aspects of blended cements. A motive and background SIS-document for the changes was elaborated. The general development in Sweden, as in most other countries, is a clear tendency to accept more of blended cements also in the more severe exposure classes.

In exposure classes XS 3 and XD 3 it is possible to use CEM I, CEM II/A-S, CEM II/A-D, CEM II/A-V, CEM II/A-LL and CEM II/A-M.
The cement strength class shall be ≥ 42,5 MPa and the W/C-ratio ≤ 0,40.

In exposure class XF 4 it is possible to use CEM I, CEM II/A-S, CEM II/A-V, CEM II/A-LL and CEM II/A-M with max 5 % “D”.
The cement strength class shall be ≥ 42,5 MPa and the W/C-ratio ≤ 0,45.

The additions slag (S), silica (D) or fly ash (V) may alternatively be added to CEM I in corresponding amount.

The salt-frost resistance for concrete in XF 4 shall be tested according to SS 13 72 44, method A (CEN/TS 12390-9).

For Swedish civil engineering structures, mainly bridges, TRV has more stringent requirements on the choice of binders. Two documents contain requirements for material and execution of civil engineering structures, namely:

- AMA Anläggning 10
- TRVAMA Anläggning 10

For bridges and tunnels the following apply:

Cements shall fulfil the requirements for CEM I in SS-EN 197-1
Cements shall at least fulfil the requirements in

- SS 13 42 02 Moderate heat cement (MH)
- SS 13 42 03 Low alkali cement (LA)
- SS 13 42 04 Sulfate resisting cement (SR)

Fly ash may be added with max 6 % in XF 4 and max 11 % in other exposure classes.

The motive for the more stringent requirements compared to the standard are the still valid reasons mentioned under 1.1 and the TRV demand for very long service life, 120 years.

# 3 DURABILITY ASPECTS AND USE OF ANL CEMENT

## 3.1 Salt-frost resistance

Frost resistance in the presence of salt is a very important property for all structures in road or sea environment. The ability of Anl cement to give the concrete a stable and very good salt-frost resistance is well documented in both field and lab tests as well as in reality. This is often attributed to the low alkali content but the coarse grinding and low water demand might also be beneficial.

It is no doubt possible to design a concrete with for instance CEM II/A-S, V, LL or M which complies with the requirements for the test results according to SS 13 72 44.It has however during laboratory tests and normal concreting been shown that the necessary air poor system in Anl concrete is less admixture demanding and less variable, than what is attained with the other cement types. So far it is considered that Anl offers the safest solution for the bridges with very long durability (min 120 years) and this is one of the reasons for TRV to continue demanding a cement of type Anl, in spite of more flexibility in the standard.

Concerning the standard it should be noted that the exposure class XF 4 is valid also for structures with shorter service lives than bridges, like parking houses, galleries, etc. For these types of structures it may not be relevant to require the solution with Anl-type of cement.

One special circumstance that has been observed in among others Swedish research is the deteriorating effect of slag on salt-frost resistance in carbonated concrete, [1]. This has implications for the choice of binders in XF 4.

## 3.2 Temperature cracking

An important factor in support of the Anl in the rather massive bridge structures is the moderate heat development, combined with a very low cracking susceptibility, confirmed in cracking frame tests both in Sweden and Germany. According to investigations by Springenschmid et al at the Technical University in Munich [2] this is not only attributed to the moderate heat, but also to an advantageous development of strength-, elasticity- and creep-properties in the early hardening. Less cracking enhances durability.

### 3.3 Sulphate and delayed ettringite resistance

Formation of ettringite in the hardened state may cause cracks and largely reduce the strength and durability properties. The strongly reduced ability of Anl cement to form delayed ettringite due to heat curing is confirmed by investigations in the Swedish Research program “High performance concrete”. [3], and is attributed to the low $C_3A$-content. This is advantageous for precast products, for instance TRV-components like railway sleepers.

### 3.4 Alkali resistance

The low alkali content of the Anl, about 0,5 % is considered valuable, since alkali-silica reactive aggregate exists in Sweden [4]. It has not been shown that the reaction leads to deleterious cracking by itself but joint action with frost attack is possible.

### 3.5 Chloride binding and corrosion

It is often claimed that cements with low $C_3A$-content, like Anl cement, have a bad chloride binding capacity and thus gives worse corrosion protection in chloride environment. Early measurements at CBI on Anl cement [5] shows however that the chloride binding capacity is good and even better compared to another Portland cement with much higher $C_3A$-content. Possibly it is the total amount of alumina that is decisive for the binding and not how much is present as $C_3A$. The Anl cement has a high $C_4AF$-content.

The question is however not finally answered and it is a fact that in the severe exposure classes XS 3 and XD 3 the addition of slag or fly ash can be used to lower the chloride intrusion rate. For corrosion initiation is however also the threshold value important. Different opinions prevail if the additions lower the threshold values or not.

## 4 CEMENTS WITH FLY ASH AND SLAG

### 4.1 Earlier experiences with blended cements

A cement with about 25 % of fly ash was introduced during the 1980:ies. The cement was used also for bridges. The experiences were however not good and production was stopped, mainly due to frequent problems with air entraining and frost resistance.

During the same period slag cement with about 65 % slag was produced, based on Swedish GGBS, for mainly massive structures like water power stations. Production was stopped due to cracking and self-healing problems with the concrete.

## 4.2 Present use of CEM II-cements

The Swedish “Byggcement”, CEM II/A-LL, is the dominant cement for house building since more than 10 years.

Based on “normal” high alkali and $C_3A$-clinker two new cements are present under development and testing. One is a CEM II/A-V with fly ash (and limestone as minor constituent), the other is a CEM II/B-M (S-LL) with slag and limestone.

The aim is for house building purpose, but air entrained concrete with CEM II/A-V is also tested in severe salt-frost environment at the SP/CBI exposure site.

## 4.2 Anl type CEM II?

Laboratory tests with a cement based on low $C_3A$ and low alkali clinker and with fly ash or slag will be conducted in a coming project together with LTH. The following should be considered.

Assure that the reliable and consistent very good salt-frost resistance with the present Anl cement is not at risk. This concerns especially

- Impact of variable LOI on dosage of air entrainer and air pore system.
- Deteriorating effect of slag on frost scaling in carbonated concrete.

Assure that the enhanced chloride diffusion resistance is not set aside by lower threshold values for start of corrosion.

Maintain low temperature cracking susceptibility, sulphate resistance and tolerance against alkali reactive aggregate.

Also the “buildability”aspect should be considered, especially the risk of slow early strength development in cold weather.

# 5 ADDITION OF FLY ASH OR SLAG TO CEM I -CONCRETE

Normal CEM I cements are often based on clinker with higher $C_3A$- and alkali-content then the Anl cement. Addition of fly ash or slag can, if the amount is high enough, make the concrete resistant to sulphates or alkali reactive aggregates, also with this kind of cement.

The high and consistent salt-frost resistance is however clearly much more difficult to achieve.

The low susceptibility to temperature cracking with Anl cement will probably also be lost.

The solution with addition of fly ash or slag to the concrete mixer also requires that these products are available. It risks therefore to be reserved for larger concrete factories in the larger city areas where silo capacity can be arranged and the right material is accessible.

# 6 FUNCTIONAL REQUIREMENTS FOR DURABILITY

It has been suggested that binder specifications should be replaced by functional requirements on the concrete. This would enable a more free choice of binders and concrete composition for civil engineering structures.

This is however a very delicate task, considering the difficulty of establishing criteria, the scatter of the available test methods and the number of methods required to assure an solution as safe as the present well known composition-prescriptive one, when it comes to all the different perspectives of bridge durability.

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# On the application of thermodynamic modelling for the prediction of the hydrate assemblage formed by blended cements

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## ABSTRACT

This paper provides a brief overview of the possibilities for predicting the hydrate assemblage and the porosity of pastes using a thermodynamic modelling software GEMS (Gibbs free Energy Minimisation Software). To be able to model blended cements with fly ash and slag the following information is required: (1) the composition of the reactive content of the OPC, fly ash and slag, (2) the reactivity of the fly ash and slag and how they affect the reactivity of OPC, and (3) the type of hydration products that can be expected to form from the binders in combination.

**Key words:** Fly ash, slag, modelling, phase assemblage.

## 1. INTRODUCTION

The ultimate goal is to be able to predict the macro-properties such as compressive strength and durability of the concrete, based on the properties of the anhydrous binders (ordinary Portland cement (OPC), fly ash and slag) as shown schematically in Figure 1. In this paper the focus is on the properties of the OPC, fly ash and slag that are needed to model the phase assemblage and the porosity, as well as the limitations and possibilities of the model.

The thermodynamic modelling software GEMS (Gibbs free Energy Minimization Software) is used for this purpose. The software was developed by PSI Switzerland for geochemical systems [1]. The PSI-GEMS thermodynamic database [2, 3] was extended for the use on Portland cement systems [4-6]. GEMS computes the equilibrium phase assemblage in a multicomponent system based on the bulk composition of the materials. It has been used to model the hydrate assemblage of amongst others Portland cement hydration [4], the effect of limestone powder additions to Portland cement [7] and the effect of changing the curing temperature [6].

To be able to model blended cements containing fly ash and slag the following information is required:

(1) the composition of the reactive content of the OPC, fly ash and slag
(2) the reactivity of the fly ash and slag, and how they affect the OPC reactivity
(3) the type of hydration products that can be expected to form from the binders in combination.

*Figure 1: Thermodynamic modelling can be used to predict the phase assemblage and porosity of the cement paste based on the properties of the anhydrous binder. This could ultimately contribute to the prediction of macro-properties such as mechanical strength and durability of the concrete. The latter indicated in grey is not part of this paper.*

## 2. THERMODYNAMIC MODELLING - REQUIREMENTS AND POSSIBILITIES

### 2.1 Properties of OPC, slag and fly ash

The properties needed to model the hydration of OPC are the mineral composition and the fineness as described in [4].

For fly ash and slag used in cement or concrete, there are certain requirements in the Norwegian regulations. NS-EN 197-1 defines two classes of fly ash cement and gives some requirements for fly ash and slag used in blended cements. For example a siliceous fly ash (V) should contain less than 10% reactive CaO, the $SiO_2$ content should be larger than 25%, and the total of CaO, $SiO_2$ and $Al_2O_3$ should be larger than 70%. A calcareous fly ash (W) should on the other hand have a reactive CaO content larger than 10%. For the granulated blast furnace slag (S) more than 75% of the mass should consist of $SiO_2$, CaO and MgO, and the (CaO + MgO) to $SiO_2$ ratio should be larger than 1. NS-EN 450-1 formulates definitions, specifications and conformity criteria for fly ash to be used in concrete. There is both a range of chemical and physical requirements that need to be fulfilled. The aim of these regulations is to guarantee that quality fly ash and slag are used in concrete production. However, additional information is needed if one wishes to understand the effect of fly ash and slag on the phase assemblage formed in a blended cement paste.

For thermodynamic modelling, one needs to know the glassy reactive content of the slag or fly ash and its composition. One way to obtain this is by performing an XRD-Rietveld analysis on the fly ash or slag to identify and quantify the crystalline phases and subtract the oxide content of these phases from the total oxide content determined by XRF [10]. The distribution of the different phases can be studied using SEM-EDS analysis. Also physical characterisation with for example a laser diffractometer to determine the particle size distribution or a SEM-BSE to study the particle shapes and/or distribution can lead to a better understanding when comparing the reactivity of different fly ashes and slags.

Figure 2 shows the effect of variations in the $Al_2O_3/SiO_2$ ratio of fly ash on the volume of phases formed as a function of time. A higher aluminate content of the fly ash will give rise to a higher amount of AFm or AFt phases formed. The effect shown in Figure 2 is however limited due to the relatively low degree of reaction of the fly ash, and the high aluminate uptake of the C-S-H (assumed molar ratio of Al/Si in C-S-H = 0.13).

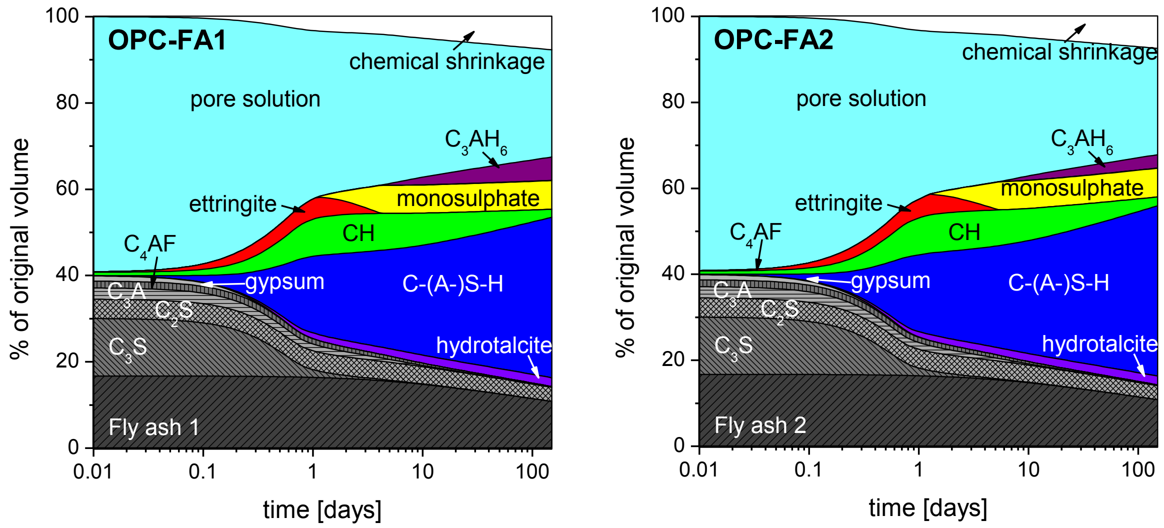

*Figure 2: The effect on the phase assemblage of variations in the $Al_2O_3/SiO_2$ ratio of fly ash in a 65%OPC+35%FA cement: FA1 ($Al_2O_3/SiO_2$ = 33%, $CaO/SiO_2$ = 18%) and FA2 ($Al_2O_3/SiO_2$ = 14%, $CaO/SiO_2$ = 16%).*

## 2.2 Kinetics of slag and fly ash reaction

In order to better understand the effect of the fly ash or slag on the phase assemblage it is important to have an idea how they influence the reactivity of the OPC and how fast they react themselves. A range of methods has been used to investigate the reactivity of OPC and/or fly ash and slag (see Table 1).

The amount of bound water evaluated with thermogravimetric analysis (TGA) has been used to evaluate the degree of reaction of the OPC. This method is however not applicable for SCM's as they tend to change the hydrate assemblage (different hydrates are formed and CH is consumed) and hence the amount of water bound per unit reacted changes. The decrease in the amount of calcium hydroxide (CH) determined by TGA in a fly ash blended cement paste has been used to evaluate the reactivity of fly ash, but care should be taken as the initial CH content of the system tends to increase due to the filler effect of the fly ash on the OPC [11, 12].

XRD-Rietveld has been used to determine the degree of reaction of the semi-crystalline clinker minerals [13], but this cannot be used to detect the amount of the amorphous glass of the fly ashes or slags reacted.

SEM-BSE combined with image analysis can be used to evaluate both the overall degree of reaction of the OPC and the degree of reaction for both fly ash and slag, given that enough images are taken to supply a statistical basis [10].

$^{29}$Si NMR can give an idea of the reactivity of Si containing phases both in OPC and slag or fly ashes [12].

Selective dissolution has been used by many researchers, but is not advised as method as it is prone to a large systematic error because certain anhydrous phases from the slag or fly ash might dissolve and certain hydration phases might not dissolve [10].

Isothermal calorimetry and chemical shrinkage are laboratory methods which allow to monitor the development of reaction of blended cements, however it is hard to differentiate the contribution of the filler effect and the actual reaction of the fly ash or slag [11-13].

*Table 1: Methods used to investigate the reactivity of OPC and/or fly ash and slag. 'V' stands for applicable,'/' for not applicable and 'V(?)' applicable but with limitations.*

| Methods | OPC | FA/slag |
|---|---|---|
| TGA - amount of bound water | V | / |
| - CH consumption | / | V (?) |
| XRD-Rietveld | V | / |
| SEM (image analysis + EDS) | V | V |
| $^{29}$Si NMR (Si phases) | V | V |
| Selective dissolution | / | / |
| Isothermal calorimetry | V | V (?) |
| Chemical shrinkage | V | V (?) |

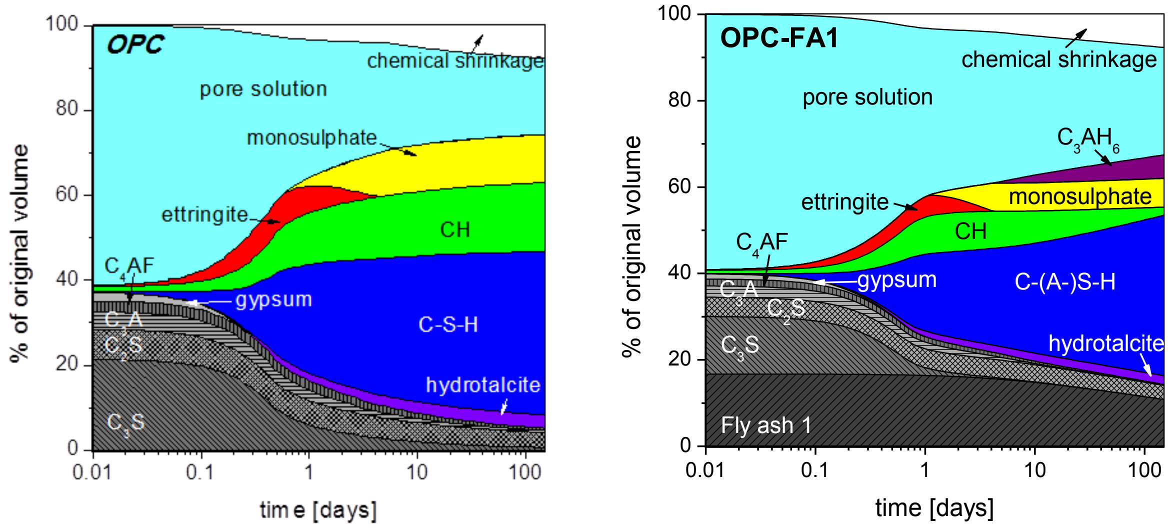

*Figure 3: Comparing the modelled hydration of a pure OPC with the hydration of the 65%OPC+35%FA1.*

When comparing the rate at which hydration products are formed in an OPC and fly ash blended cement (see Figure 3), it is clear to see that fly ash cements tend to react slower than a pure OPC due to the slow reaction of the fly ash. In order to be able to foresee the amount and the type of hydration products formed with time, it is important to have an idea of the reactivity of both OPC and fly ash or slag in blended cements.

## 2.3 Type of hydration products formed

To be able to predict the hydration products formed one has to have a hunch of what kind of hydrates to expect. One of the major black boxes for the modelling of hydration products is the main hydration phase, C-S-H. For cements containing fly ash or slag, it is known that the Ca/Si ratio of the C-S-H tends to decrease with reaction time. Over time C-S-H also incorporates Al, reducing the potential amount of AFm and AFt phases formed. The reduction of the pH in blended cements over time has also been attributed to the uptake of alkali in the C-S-H. These variations in the C-S-H composition, depending on the type of fly ash or slag used, the reaction time, curing temperature and replacement level [12], are difficult to incorporate in the model. For now, a solid solution of jennite and tobermorite is used independent of the before named factors. There is currently a lot research going on to improve the C-S-H model to take in account the variations.

Figure 4 shows that a reduction in the Al/Si ratio of the C-S-H leads to changes in the type and amount of AFm and AFt phases predicted for a 65%OPC+35%slag cement.

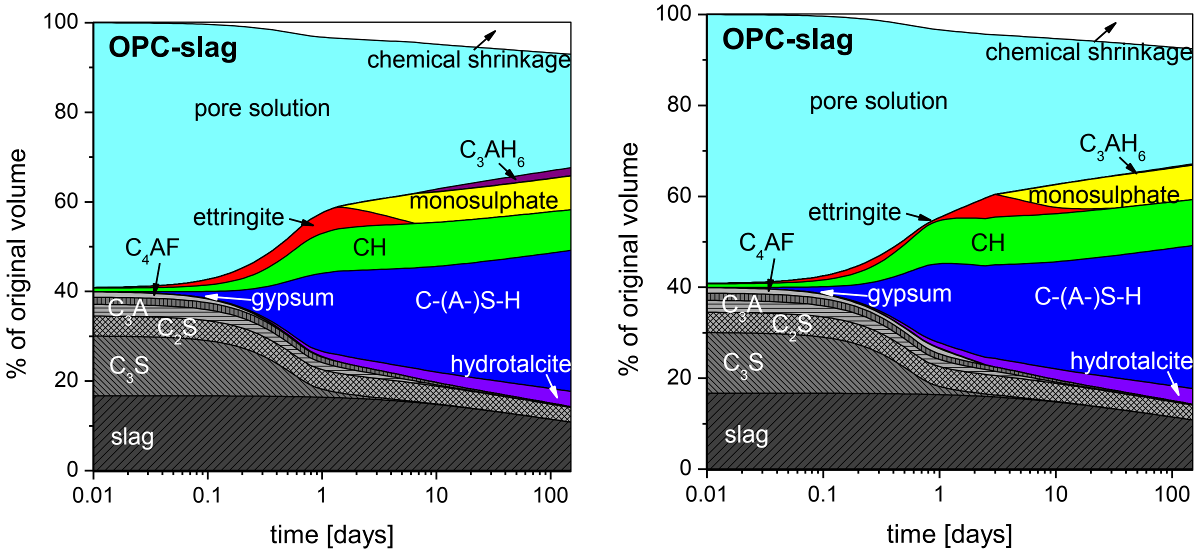

*Figure 4: The effect of changes in the Al/Si ratio of the C-S-H on the predicted hydrate assemblage of a 65%OPC+35%slag cement: left: Al/Si = 0.13, right: Al/Si ratio = 0.20.*

Not only the phase assemblage, but also the total volume of the capillary porosity can be modelled using thermodynamic modelling. *Figure 4* shows the volume change of the phases during hydration. The graphs are based on thermodynamic modelling of the phases present and knowledge on their molar volume and provide information on both water filled ("pore solution") and potential empty ("chemical shrinkage") capillary porosity. As for the modelling of the phase assemblage, the molar density (and gel porosity) of the C-S-H is at present the most uncertain parameter. It should be noted that the thermodynamic modelling does not give information on the pore size distribution, nor the connectivity of the porosity. As illustrated in [14] both the binder composition and the curing conditions may have a significant impact on the porosity. Pastes with slag were observed to have reduced threshold pore sizes (reduced connectivity) when compared to pastes with same porosity from ordinary Portland cement alone (2 years, 20°C, porosity measured by mercury intrusion porosimetry MIP).

## 3. CONCLUSION

In order to be able to predict the phase assemblage and the porosity formed in cement pastes with fly ash or slag cement using thermodynamic modelling one needs information about:

(1) the composition of the reactive content of the OPC, fly ash and slag
(2) the reactivity of the fly ash and slag, and how they affect the OPC reactivity
(3) the type of hydration products that can be expected to form from the binders in combination.

There are challenges regarding each of these points as discussed in the paper. However, thermodynamic modelling is a powerful tool which can help us on the way to better understand the link between characteristics of binders and their impact on the hydrate assemblage and capillary porosity and hence also the macro properties such as strength and to some extent durability.

## ACKNOWLEDGEMENTS

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# The Norwegian System for Performance Testing of Alkali Silica Reactivity (ASR) – Some Experiences

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## ABSTRACT

In 1996, the Norwegian 38°C concrete prism test was specified in the Norwegian guidelines [1] for ASR performance testing of aggregates (alkali threshold) and/or binders (i.e. various cements added any SCMs or other mineral admixtures). Revised guidelines were published in 2004-2005 [2-4]. Up to 2010, about 160 performance tests had been carried out at SINTEF and Norcem. Experiences gained from these tests were published by Lindgård et al. in 2008 [5] and 2010 [6]. A main conclusion drawn from these tests is that the Norwegian concrete industry has successfully used the performance test as a flexible tool to be able to utilize alkali reactive aggregates, which are widely spread all over Norway. The last two years, about 15 additional performance tests have been initiated at SINTEF, primarily to document the effect of new fly ashes co-grinded in the Norcem CEM II/A-V cements.

**Key words:** alkali-silica reactions, performance testing, Norwegian experiences, fly ash, slag (ggbfs)

## 1 INTRODUCTION

### 1.1 Background

Alkali-Silica Reaction (ASR) was recognized as a deterioration problem in Norway about 1990. Since then, several comprehensive national research projects have been carried out on this subject. These projects have strongly focused on test methods for aggregates and corresponding criteria for the prediction of ASR as observed on Norwegian concrete structures. The research projects have resulted in reasonably reproducible test methods regarding ASR of Norwegian aggregates.

## 1.2 The Norwegian system for approval based on performance testing

In 1996, the Norwegian Concrete Association published a national guideline on ASR (“NB 21”) [1]. Based on knowledge gained after 1996, and the fact that the publication now is a harmonised normative reference document to the new concrete materials standard, NS-EN 206-1 [7], a revised version of the publication was provided in 2004 [2, 3].

The 2004 edition of “NB21” is divided into two major parts. Part 1, “Specifications”, describes in formal terms the mandate and the use of the publication, and how concrete constituents and concrete recipes shall be tested and evaluated with respect to potential ASR. Individual aggregates and blends of aggregates shall be evaluated by the petrographic analysis as a first step. The evaluation based on results from these analyses can be reassessed by the 80°C AMBT, while the 38°C concrete prism test (CPT) can be used to reassess the evaluation from any of these tests. For the evaluation of binders and concrete compositions (incl. mortars and shotcrete), only the CPT (prism size 100x100x450 mm) can be used.

The three methods are described in detail in a corresponding publication from the Norwegian Concrete Association (“NB32”) [4]. “NB32” also gives rather detailed requirements to laboratories that aim to be approved to run the Norwegian ASR tests.

Part 2 of “NB21” gives advisory guidelines for how the concrete industry can fulfil the requirements given in part 1. It also provides a survey of binders and corresponding alkali contents documented to be suitable for production of ASR resistant concrete containing all types and amounts of Norwegian reactive aggregates. This survey is updated whenever new binders obtain satisfactory documentation – see www.betong.net (*comment: click on “Publikasjoner”*).

Based on extensive laboratory performance testing and comprehensive calibration of results against field behaviour [8, 9], “NB21” states that all CEM I binders shall be considered to be suited for production of non-reactive concrete containing all types of alkali reactive Norwegian aggregates up to an alkali content of 3.0 kg $Na_2Oeq/m^3$ of concrete. If alkali reactive aggregates are to be used in CEM I based concretes with a higher alkali content or in concretes containing other binders, the Norwegian regulations require performance testing of the actual “job mix” or the actual binder. In such general testing of different binders’ ability to prevent development of alkali silica reactions, the binders are tested in concrete containing a specified aggregate composition [4] (see Table 1) that for Norwegian conditions is considered to be “worst case” with respect to alkali reactivity (i.e. reacts at low alkali levels and gives a very high prism expansion when tested in the CPT). Thus, the testing might give a general approval for using the tested binders in combination with all Norwegian alkali reactive aggregates, which in general are assumed to be less reactive than the reference reactive aggregate combinations (see Table 1) applied in the performance tests.

The validity of documentation supplied by performance testing is limited to concrete with composition considered to be no more reactive than was the concrete used for the testing. The reactivity is considered to increase if:

- The concrete alkali content increases *(comment: For performance tested materials, extra fly ash or silica fume may be added the cement or the concrete mix without any further documentation, even if these additions contribute with supplement alkalis).*
- The content of pozzolanic material or other SCMs decreases.

- The content of reactive rock types increases more than the upper limit specified in the publication *(comment: No pessimum effects have been documented for any Norwegian aggregate – opposite to the experience gained e.g. in Denmark with opaline flint [10]).*

The acceptance criteria for different types of binders and concrete recipes are differentiated when the CPT results are assessed. In general it can be said that:

- CEM I binders and CEM I based concrete compositions containing no pozzolans or other SCMs shall be considered non-reactive if showing 1 year expansion less than 0.050 %.
- CEM I based concrete compositions containing silica fume, concretes based on the fly ash blended CEM II/A-V cement produced by Norcem in Norway (co-grinding of PFA and clinker) and / or blends of this cement and CEM I shall be considered non-reactive if showing 1 year expansion less than 0.030 %.
- Concrete recipes based on other binders than those mentioned above shall be considered non-reactive if showing 1 year expansion less than 0.030 % and at the same time 2 years expansion less than 0.060 %.

A performance test shall be based on one or more mixes. If based on more than one mix, test results shall be plotted in an expansion versus alkali content-diagram as illustrated by Figure 1.

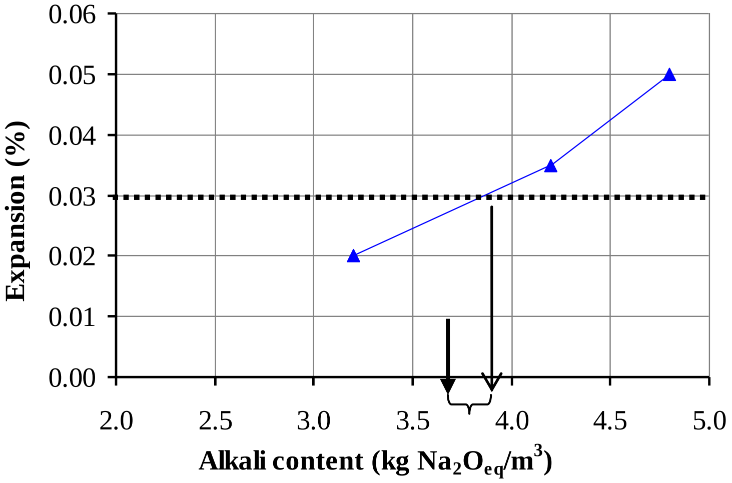

*Figure 1 - Principle diagram for determination of acceptance limit for alkali content based on performance testing according to Norwegian regulations. The dotted line represents the critical expansion limit for PFA binders after one year of exposure. The bracket represents the "safety factor" amounting to 0.2 kg $Na_2O_{eq}/m^3$ of concrete. In the current example, the critical alkali limit is (3.85-0.20) 3.65 kg $Na_2O_{eq}/m^3$ of concrete.*

Based on the assumption that a linear relation exists between expansion and alkali content, straight lines connecting the points shall be drawn. If a connecting line and the line illustrating the accepted limit for expansion cross each other, the alkali content limit value for acceptance of non-reactivity is given by the alkali content at the point of intersection subtracted a "safety factor" amounting to 0.2 kg $Na_2O_{eq}/m^3$ of concrete. If the above-mentioned crossing of lines does not occur, the alkali content limit value for acceptance of non-reactivity shall be:

- 3.0 kg $Na_2Oeq/m^3$ when all the mixes show expansions exceeding the acceptance value.
- Equal to the highest individual alkali content used within the mixes involved when all the mixes show expansions less than the acceptance value.

Internationally, a too high extent of alkali leaching is reported to be one of the main sources of error in connection with accelerated performance testing (see e.g. Thomas et al. [11]), leading to a correspondingly reduced alkali content within the test prisms during the test. Consequently, a too low expansion may be obtained, negatively influencing the laboratory/field correlation. Despite this fact, no specific "safety factor" (beyond the 0.2 kg $Na_2Oeq/m^3$ alkalis of concrete discussed above) is included in the Norwegian regulations to compensate for the (so far limited documented) amount of alkalis that may leach out from the test prisms in the CPT during the one to two years exposure period. However, alkali leaching is currently focused on in on-going national research activities, as well as in the RILEM task group 219-ACS-P "Performance testing". This is also the case regarding the question if some aggregate types may release alkalis into the concrete pore water during the test period.

# 2 REVIEW OF NORWEGIAN PERFORMANCE TEST SERIES

## 2.1 Available test results

Since performance testing by use of the Norwegian 38°C CPT started in Norway in 1996, the detailed testing procedure has been unchanged [4]. Only a few testing laboratories are approved to perform such performance testing on a commercial basis. As part of the PhD study of Jan Lindgård, all available results from the performance test series performed up to 2010 by the two most experienced approved Norwegian laboratories, SINTEF Building and Infrastructure (Trondheim) and Norcem (Brevik) have been compiled and evaluated [5, 6]. SINTEF have primarily performed the testing on a commercial basis for the industry, while Norcem mainly have tested the performance of various cements in trade or under development [12-16]. All the about 30 concrete prisms test series being part of the PhD study of Bård Pedersen [17, 18] are also included in the review. SINTEF performed all the test series in his study, focusing of the possible mitigating effects of different filler types on ASR.

In total, the review of the tests up to 2010 included results from 161 performance test series. Tables 1 and 2 give an overview of the different aggregate types and binder types tested. The duration for the finalised test series varied from one to twelve years. The last two years, about 15 additional performance tests have been initiated at SINTEF, mainly to document the effect of new fly ashes added to the Norcem CEM II/A-V cements (produced by co-grinding of fly ash and clinker).

*Table 1 - Overview of aggregate types included in the reviewed performance test series executed in Norway in the period 1996-2010 [5, 6]*

| Aggregate type | | Number |
|---|---|---|
| Fine (0-5 mm) | Coarse (5-20 mm) | of tests [1] |
| Reference-I (NR) [2] | Reference-II (R) [3] | 26 |
| Reference-III R [4] | Reference-II (R) [3] | 49 |
| Reference-IV R [5] | Reference-II (R) [3] | 7 |
| Reference-IV R [5] | Reference-I (NR) [2] | 26 |
| Different types [6] | Different types [6] | 50 |
| Recycled glass (R) | Recycled glass (R) | 3 |
| | Sum | 161 |

[1] 119 of the tests are performed at SINTEFs laboratory (include the 29 tests being part of Bård Pedersens PhD study [17,18]). The remaining 42 tests are performed by Norcem.

[2] Non-Reactive (NR) natural gneiss/granite aggregate.

[3] Reactive (R) chrushed cataclasite.

[4] Natural aggregate (R) with claystone, siltstone and phyllite as the main reactive rock types.

[5] Natural aggregate (R) with mylonite, cataclasite, greywacke and phyllite as the main reactive rock types.

[6] Primary alkali silica reactive aggregate types. 27 of the mixes include a crushed mylonite [17,18].

*Table 2 - Overview of binder types included in the reviewed performance test series executed in Norway in the period 1996-2010 [5, 6]*

| Binder type | Total number of tests | Number of the tests added CSF [5] |
|---|---|---|
| CEM I [1] | 51 | 8 |
| CEM I + CEM II Portland fly ash cement [2] | 45 | 22 |
| CEM II Portland fly ash cement [2] | 26 | 9 |
| CEM II Portland slag cement [3] | 7 | --- |
| CEM I + fly ash added separately | 5 | --- |
| CEM I + added LWA fines | 4 | --- |
| CEM I + added different filler types [4] | 22 | --- |
| CEM I + other admixture added | 1 | --- |
| Sum | 161 | 39 |

[1] All the cements, except the Portland slag cement, are produced by Norcem (part of the Heidelberg Cement Group). Different types of CEM I have been tested.

[2] CEM II/A-V including about 20 weight-% fly ash of the binder.

[3] CEM II/B-S including at least 32 % ggbfs.

[4] Most filler types were produced from alkali reactive aggregates [17,18].

[5] CSF = Condenced Silica Fume.

The 161 test series include some "job mixes" and some mixes to determine the critical alkali limit for various aggregate types. However, most of the performance test series have aimed to document different binder combinations ability to prevent ASR. Reference reactive aggregates were used in these tests series. In addition to different CEM I cements, the binders tested included pulverized fly ash (PFA), condensed silica fume (CSF), ground granulated blast furnace slag (ggbfs), light weight aggregate fines and/or different filler types (mainly produced from alkali silica reactive rock types). The water/binder ratio in the test series varied mainly between 0.45 and 0.48. If needed to boost the alkali content, NaOH was added to the mixes.

## 2.2 Alkali leaching

Since 2007, SINTEF have systematically performed analyses to document the extent of alkalis leached out from the prisms in the Norwegian CPT during the one to two years exposure period. To avoid contamination, all testing equipment and storage containers are washed properly and a new lining is applied before new test series are started. At every standard measuring points of time, a 20 ml sample of the water in the bottom of each storage container is collected. Before each sampling, the total amount of water is calculated by measuring the depth of the water in the centre of each container. A depth versus volume ratio has previously been established for the applied type of storage container by successively adding a known quantity of water and measure the corresponding water depth. If some of the water has evaporated since the last measurement, water is added after sampling.

The content of alkalis, $Na^+$ and $K^+$, has been measured by use of flame atomic absorption spectroscopy (FAAS). Based on these measurements, the total content of alkalis leached out from the concrete prisms has been calculated.

# 3 RESULTS AND DISCUSSION

Selected results from the performance testing, including documented rate and extent of alkali leaching, are presented and discussed in two papers [5, 6]. In this document, only some examples from performance testing of some blended cements are presented.

## 3.1 Performance testing of binders

As shown in Table 2, most of the performance test series have aimed to document different binder combinations ability to prevent ASR. About 70 of these test series have included Norcem “Standard FA” cement, a CEM II/A-V Portland - fly ash cement with a PFA content of approximately 20 % by weight of binder. All the fly ashes used the last 15 years are carefully selected in order to have good ASR mitigation properties. In contrast to usual CEM I - PFA combinations, the Norcem “Standard FA” cement is manufactured by co-grinding clinker and PFA, a process that has shown to enhance the well known ASR mitigating effect of fly ash [19]. An example of the effectiveness of this cement to suppress ASR is given in Figure 2. PFA constitutes about 80 kg/m$^3$ of the binder. All the alkalis in the fly ash are included in the calculated total alkali content of the concrete mixes. The expansion of these mixes increases with increasing alkali content from 5.0 to 8.5 kg $Na_2Oeq/m^3$ of concrete, obtained by boosting with NaOH. Based on such performance testing, all the Norcem “Standard FA” cements with various selected fly ashes have given acceptance alkali limits equal to or higher than 6.5 kg $Na_2Oeq/m^3$ of concrete, and may thus be used in combination with all Norwegian concrete aggregates up to this documented alkali limit.

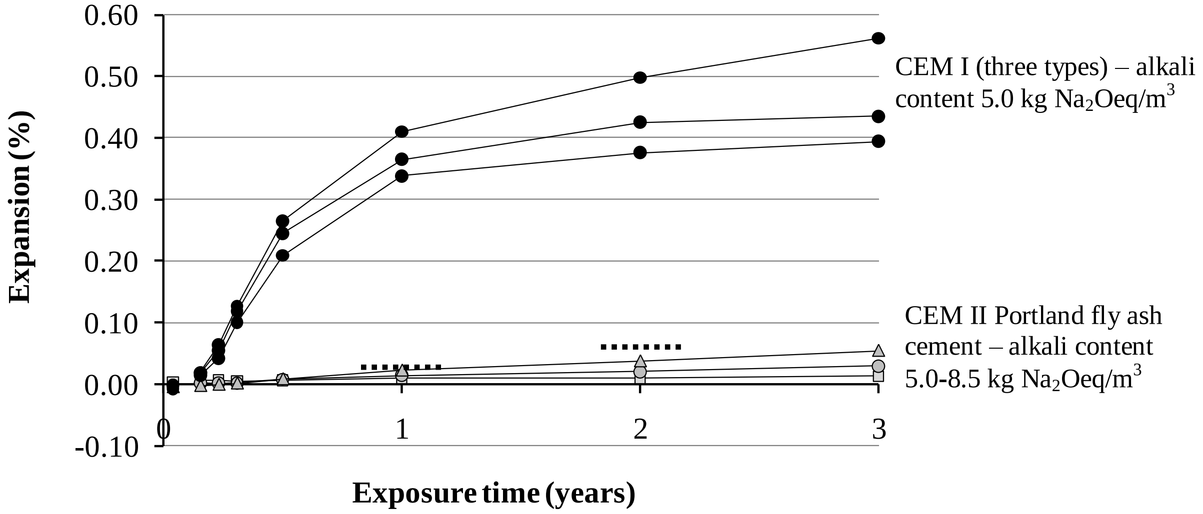

*Figure 2 - Expansion versus exposure time for six binders tested with the aggregate combination Reference-I (non-reactive fine) + Reference-II (reactive coarse) - see Table 1. The CEM II Portland - fly ash cement contains 20 % PFA (80 kg/m$^3$ of concrete). The dotted lines drawn at 1 and 2 years, respectively, represent critical limits for concretes with binders containing fly ash, condensed silica fume or ggbfs.*

Even though a one year testing time is required (two years for special binders – see section 1.2), Norwegian cement – and concrete producers have frequently executed such performance tests. The aim has been to achieve approval for using different binder combinations (e.g. a CEM II Portland – fly ash cement) and/or possible new pozzolanic material (e.g. fillers produced from reactive rock types) in combination with various alkali reactive Norwegian aggregates. In this way, a number of commercial concrete recipes might be pre-documented, giving the concrete producers flexibility with respect to fulfilling the ASR requirements in the Norwegian regulations.

### 3.2 Alkali leaching

According to Thomas et al. [11], the problem with alkali leaching from specimens stored over water in sealed specimens was first reported by Blanks and Meissner in 1946 [20]. They detected a build up of alkali ions in the water at the bottom of the containers in which mortar bars were stored, and explained this based on water condensing on the surface of the bars and running down the bars into the reservoir below, thereby providing transport of the alkalis. Due to this alkali leaching, the alkali content within the test prisms is reduced, leading to a drop in the pH of the pore water. Consequently, less silica is being dissolved from the aggregates and the extent of ASR is reduced, resulting in a too low prism expansion.

Several parameters may influence the extent of alkali leaching, among them prism size, storage conditions and concrete composition, as discussed in the recently published review of parameters that might influence ASR performance testing [21].

Figure 3 shows the cumulative extent of alkali leaching for 30 SINTEF CPT series, where the alkali content measured in the water in the bottom of the storage containers is recalculated to represent the reduction in alkali content in % compared to the total alkali content in the concrete at the time of mixing (includes all alkalis in the cement and in any mineral - and chemical admixtures, but excludes any alkalis that possibly may be released from the aggregates). As can be seen, the rate of alkali leaching is highest the first three to six months of exposure. After one year of exposure, from 0.1 to 0.9 kg $Na_2Oeq$ alkalis per $m^3$ of concrete are leached out from the prisms with size 100x100x450 mm, representing 2-17 % of the original alkali content in the concrete. Correspondingly, Thomas et al. [11] reported that 35 % of the alkalis originally in prisms of size 75x75x300 mm were leached out after 1 year, and as much as 20 % after just 90 days, i.e. about twice as much as the highest values from the larger Norwegian concrete prisms.

The presented results thus show that use of relatively large concrete prisms in the Norwegian CPT secure a rather low extent of alkali leaching compared to corresponding concrete prism tests applying smaller prisms (as most internationally concrete prism tests do). Still, the possible influence of alkali leaching on the measured expansions in the NCPT cannot be neglected. Thus, the leaching issue are being looked further into.

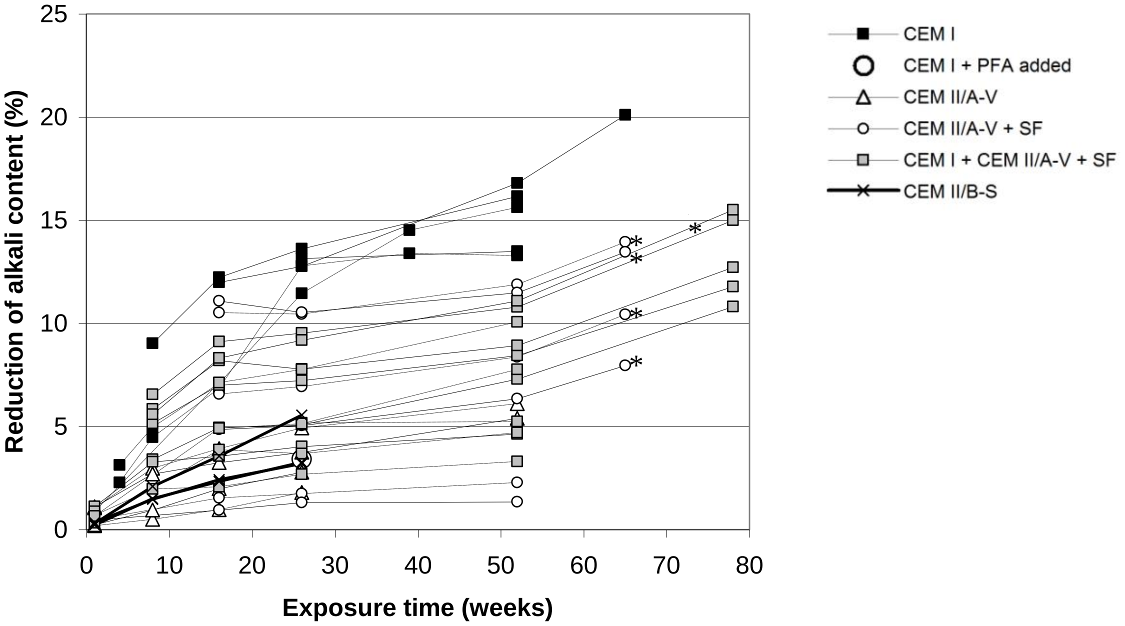

*Figure 3 - Alkali content measured in the water in the bottom of storage containers, re-calculated to represent the reduction in alkali content in % compared to the total alkali content in the concrete at the time of mixing. The solid-drawn lines represent concrete mixes in which NaOH is added to increase the alkali content. The dotted lines represent concrete mixes without extra NaOH added. (* = "shotcrete")*

Any alkalis absorbed by the lining inside the storage containers are not included in the presented results. Later tests performed at SINTEF show that the extent of alkalis absorbed by the lining after one year of exposure constitutes less than 2.5 % of the total alkali content in the concrete at the time of mixing (CEM I, w/c-ratio 0.45).

Similar as Bokern [22] reported, OPC (CEM I) seems to be most vulnerable to alkali leaching, while some of the mixes with fly ash cement (CEM II/A-V) show the lowest extent of alkali leaching. Also mixes with the CEM II/B-S cement containing 33 % ggbfs show a low extent of alkali leaching (3-5 %) after 26 weeks of exposure.

As mentioned in section 1.2, no specific “safety factor” (beyond the 0.2 kg $Na_2O_{eq}/m^3$ alkalis of concrete discussed above) is so far included in the Norwegian regulations to compensate for any alkalis that may leach out from the concrete prisms during the one to two years exposure period. However, some extra security is already built in these regulations when testing binders, since most alkali reactive aggregate types in common use in Norway are far less reactive than the reference “worst case” alkali reactive aggregate combinations applied for performance testing of binders. In addition, most commercial concretes containing SCMs will normally contain less alkalis than the critical alkali limits documented for various binders. Norcem has also declared “upper alkali limits” for their cements to be used for calculating the concrete alkali content according to the Norwegian regulations.

## 4 CONCLUSIONS

During the last 15 years, about 175 performance tests have been performed by the two most experienced approved Norwegian laboratories at SINTEF and Norcem. Most performance tests have aimed at documenting different binder combinations ability to prevent ASR. In these tests, reference reactive aggregates are used. Based on the review of the results from these tests [5, 6], the following conclusions may be drawn:

- Despite the long testing time required (1-2 years), the Norwegian system for performance testing has proven to be an advantageous and flexible tool to document critical alkali limits for binders and aggregates.
- The repeatability obtained at SINTEF for the Norwegian CPT is in general very good.
- By using the Norcem Standard-FA cement (CEM II/A-V), containing about 20 % PFA, a general acceptance alkali limit of 6.5 kg $Na_2O_{eq}/m^3$ of concrete (including all the alkalis in the fly ash) is approved in combination with all Norwegian aggregate types in common use.
- From 0.1 to 0.9 kg $Na_2Oeq$ alkalis per $m^3$ of concrete are leached out from the concrete prisms after one year of exposure, representing 2-17 % of the original concrete alkali content. The highest extent of alkali leaching measured from these Norwegian CPT prisms represents about half as much as reported from smaller prisms, e.g. as applied in ASTM C 1293 CPT [23].
- The possible influence of alkali leaching on the measured expansions in the Norwegian CPT cannot be neglected, even though rather large concrete prisms are used.
- No specific “safety factor” (beyond a “general safety factor”) is included in the Norwegian regulations to compensate for any alkalis that may leach out from the prisms in the NCPT. However, some extra security is already built in these regulations when testing binders (see 3.2).

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# Effects of Slag and Fly Ash in Concrete in Chloride Environment – Research from The Netherlands

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## ABSTRACT

Research is reported on concrete made with blast furnace slag and fly ash related to chloride induced reinforcement corrosion, carried out in The Netherlands, where slag has been used in cement for almost a century. Results are presented from field studies on concrete in marine environment and laboratory studies involving chloride exposure. Chloride surface content, diffusion coefficient, electrical resistivity, critical chloride content and corrosion rate are discussed. Both slag and fly ash concrete show improved behaviour compared to Ordinary Portland cement in aggressive environments, in particular where penetration of chloride presents the risk of reinforcement corrosion.

**Key words:** durability, concrete, chloride, corrosion, diffusion, resistivity, blast furnace slag, fly ash

## 1. INTRODUCTION

### 1.1.1 General

Presently various reasons exist for an increasing interest in "blended cements" that incorporate other reactive mineral components than Portland clinker: usage of industrial by-products and waste materials, thus saving precious raw materials; reduction of Portland clinker usage in order to reduce $CO_2$ emission; and increased durability, in particular in chloride contaminated environment, thus increasing the service life of structures. Using ground granulated blast furnace slag (GGBS or BFS, for simplicity further called *slag*) as a cement component in The Netherlands dates back to the first half of the twentieth century. Later, pulverised fuel ash or *fly ash* from powder coal fired power stations has become increasingly used in cement. Both slag and fly ash concrete showed improved behaviour compared to Ordinary Portland cement in aggressive environments, in particular where penetration of chloride presents the risk of reinforcement corrosion. After briefly relating the history of slag use in The Netherlands, this paper focuses on research carried out in The Netherlands on slag and fly ash with regard to chloride transport and reinforcement corrosion, both in the field and in the laboratory.

## 1.2 History of slag and fly ash use in concrete in The Netherlands

This brief historical overview is based on [1,2]. Slag cement production started in Germany in 1888, from which slag cement was imported. Between 1919 and 1930 slag cement was used for building the North Sea canal locks at IJmuiden; testing showed the good resistance to sea water. In 1931 a slag cement plant was established at IJmuiden in collaboration between steel and cement producers. The regulations issued between 1912 and 1962 reflect the changing attitude towards slag use in concrete. In GBV (regulations for reinforced concrete) 1912, slag was prohibited in concrete; in GBV 1918 high slag percentages (75%) were prohibited in reinforced concrete, but 30% slag was allowed. Since 1930 using slag cement was only allowed if client and contractor agreed so in advance; this remained the position in the 1930, 1940 and 1952 regulations. In the 1962 code the choice of cement type was free; it was stated that slag cement has better characteristics in aggressive environment than Portland cement. In 1984, slag cement was recommended and Portland was discouraged for use in aggressive environments. The 1986 concrete technology standard, in which environmental (exposure) classes were introduced, recommended using slag cement with high sulphate resistance, i.e. with at least 65% slag, for marine environment. What is now called CEM III/B 42.5 LH HS (or most recently: SR), with typically 70% slag, became the dominant cement type in the 1970s. In The Netherlands, about 10 million cubic metres of slag cement concrete are produced annually, in particular for concrete cast in situ. The low heat of hydration is seen as a big advantage with regard to early age cracking. Fly ash has been used since the 1980s in CEM II/B-V with typically 27% replacement level of clinker.

Traditionally slag and fly ash were intermixed with clinker in the cement plant and sold as “cements”. The manufacturer would carefully compose these products to have similar 28 day strength as Portland cement, typically with 32.5 or 42.5 MPa of (mortar) compressive strength. In the 1990s CEM III/A 52.5R was introduced, with 52-57% slag, aimed at the precast industry, with increased early strength. Slag cements contain typically 0.6% of $Na_2O_{eq}$. Recently, separate slag for addition to Portland cement in the concrete mixing plant has become available.

Since the 1980s, The Ministry of Infrastructure regulations require concrete based on cements with at least 50% slag or 25% fly ash (for precast concrete only), among others for preventing deleterious ASR [3]. For reference to practice in other countries, traditional concrete compositions for aggressive environments (XD, XS) involve about 340 kg cement per cubic meter, a target w/c of 0.43 and rounded siliceous aggregate of 32 mm maximum size.

## 2. SLAG CEMENT RESEARCH RELATED TO CHLORIDE PENETRATION AND CORROSION

A lot of independent research has been devoted to slag cement in concrete and its durability over the last 40 years, both in the field and in the laboratory. Here the focus is on chloride and corrosion related research carried out in The Netherlands. This is not intended to play down the importance of pioneering work elsewhere in the laboratory [4] and studies based on field exposure [5,6,7]. In the 1970s durability was investigated of structures in marine environment [8]. Slag cement concrete appeared to perform very well, with hardly any visible corrosion in about 50 structures up to 63 years of age. Carbonation was found to be 5 mm or less in the large majority. Five structures were cored and chloride profiles determined. Chloride diffusion coefficients were found to be lower for slag cement than for Portland cement, by a factor of 10 to 16 [1]. Exposure for 16 years of concrete prisms submerged in the North Sea showed that slag cement had much lower chloride penetration than Portland cement concrete [9]. Results from chloride profile analysis and electrical resistivities are reported in Table 1. An overview was published including examples of slag in structures in the Middle East, underpinning its durability [1].

*Table 1 Chloride diffusion coefficients and surface contents from profile fitting to prisms submerged for 16 years in the North Sea [9]*

| | CEM I | CEM III/B | note |
|---|---|---|---|
| $D_{Cl}$ (*$10^{12}$ $m^2/s$) | 1 - 3 | 0.3 | CEM I: depending on w/c, curing and age at start of exposure |
| $C_s$ (% by mass of cement) | 3.5 - 5 | 2.5 - 5 | depending on curing and age at start of exposure |
| Resistivity (Ωm) | 120 - 155 | 400 - 1000 | depending on curing and age at start of exposure; CEM I depending on w/c |

In depth investigation in the early 2000s of six marine structures of up to 40 years age showed that chloride penetration was consistently slow in slag structures [10]. An overview of results from chloride penetration profile fitting the error function solution of Fick's second law of diffusion is given in Table 2.

*Table 2 Overview of chloride penetration results from six marine structures [10]*

| Structure, age (year) | $D_{Cl}$ (*$10^{12}$ $m^2/s$) | $C_s$ (% by mass of cement) | note |
|---|---|---|---|
| Pier, 40 | 0.14 - 0.28 | 3 | CEM I, low w/c; higher splash zone, sheltered from rain |
| Pier, 40 | 0.33 | 3 | CEM III/B, higher splash zone, sheltered from rain |
| Barrier, 40 | 0.12 | 2.8 | CEM III/B; lower splash zone |
| Barrier, 20 | 0.24 | 2.2 - 5 | CEM III/B; $C_s$ depends on height above sea level |
| 3 harbour quays, 20 - 33 | 0.12 - 0.19 | 3 - 4 | - |

In the laboratory, various durability and corrosion related properties of slag cement concrete have been investigated since the 1980s, including electrical resistivity [11] and its relationship to chloride transport [12], corrosion rates with mixed in chloride [13] or penetrated chloride [14], see also [15, 16]. Prisms with embedded steel electrodes were cast in 1998 with four binder types (Portland, Portland fly ash, slag and composite cement, with slag and fly ash) and three w/c's (0.40 – 0.55). They were subjected to half a year of cyclic wetting with salt solution and drying, simulating de-icing salt exposure. Subsequently, they were stored in wet and semi-dry environment and outdoors for two more years. Steel potential, corrosion rate (by linear polarisation resistance) and resistivity were monitored. Chloride profiles were determined after half a year and after 2.5 years and fitted. Chloride surface contents and diffusion coefficients are shown in Figure 1 [14, 17]. Exposure was continued since 2004 on an open roof and resistivity was again measured in 2010 [18]. Development of resistivity over 11 years is shown in Figure 2.

Summarising this lab work, slag cement concrete was shown to have higher electrical resistivity and lower corrosion rates than Portland cement concrete under comparable conditions of chloride and moisture. The higher electrical resistivity of slag cement concrete correlated with lower chloride diffusion coefficients.

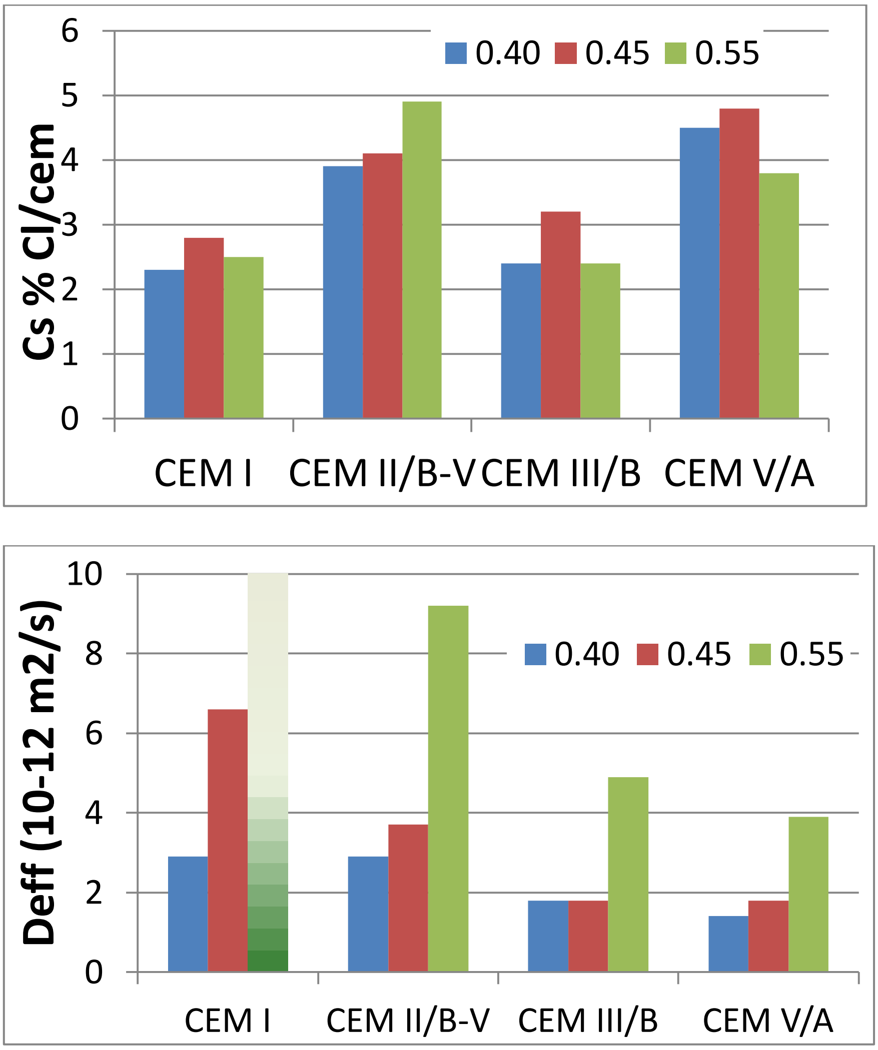

*Figure 1 Chloride surface contents (top) and diffusion coefficients (bottom) after 26 weeks salt solution/drying cycles in concrete prisms [14, 17]; note: CEM I 0.55 Deff is out of scale; value approx. 140 * $10^{-12}$ $m^2/s$*

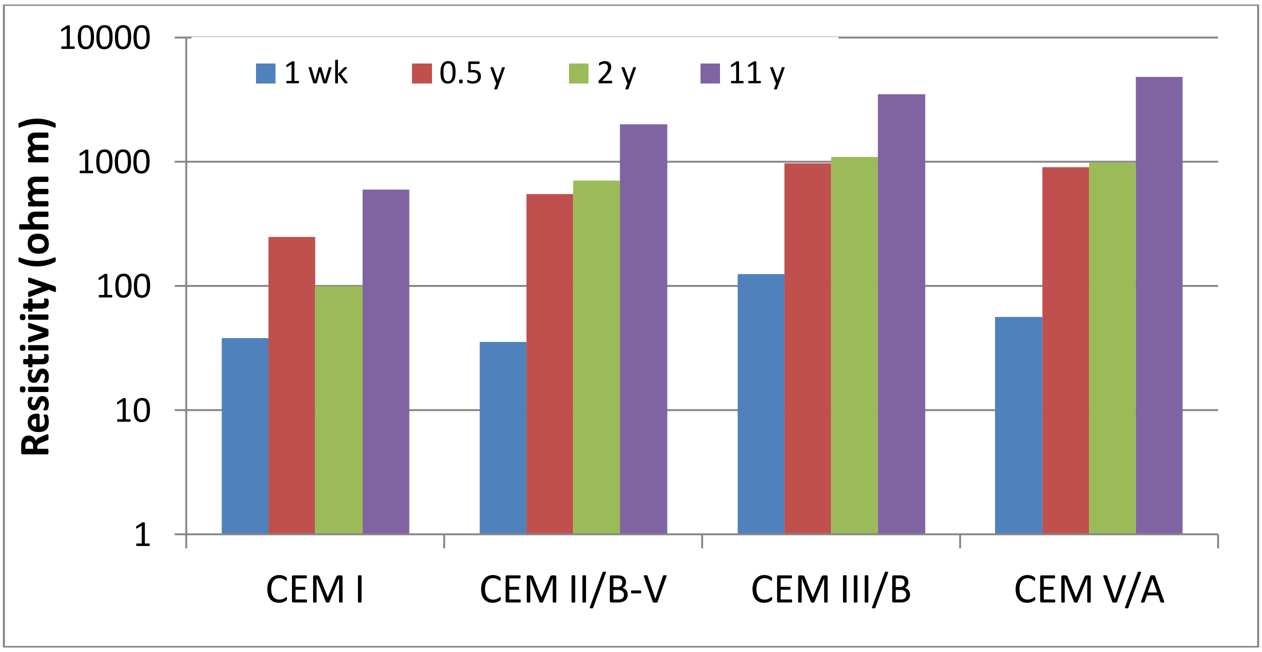

*Figure 2 Electrical resistivity of concrete with four binders and w/c 0.45 during outdoor exposure from 1 week until 11 years age, after [14,17,18]; note: Y-axis log scale*

In the 1990s, a practical accelerated test method for chloride penetration was developed in Scandinavia, NTBuild 492 or Rapid Chloride Migration test, RCM [19, 20, 21]. This method was adopted as an important element of service life evaluation and a method for quality control based on resistivity was proposed [22]. Parallel development of probabilistic service life modelling will not be addressed here [22]. However, the combination of rapid chloride migration testing and quantitative service life design requirements stimulated testing of large numbers of concrete compositions. Concrete with various binder was tested for RCM at ages up to 3 years [23]. Regulations committee CUR VC81 collected about 500 test results obtained from a wide variety of concrete compositions used in the field, a.o. in the Green Heart tunnel [24]. They were among others analysed for the influence of w/b, see Figure 3. Analysis showed that there is a linear relationship between w/b and chloride migration coefficient, with a slope and intercept that strongly depend on binder type. The dependency of the migration coefficient on w/b is much smaller for slag cement concrete than for Portland cement [25, 26]. Similar dependencies on w/b were found in Scandinavia [27] and Germany [28]. This implies that small deviations from the target w/c have a small effect on the migration coefficient for slag cement concrete, making it more tolerable for production related fluctuations. The results were used to underpin a Guideline for simplified (semi-probabilistic) service life design in XS/XD environment [25, 26].

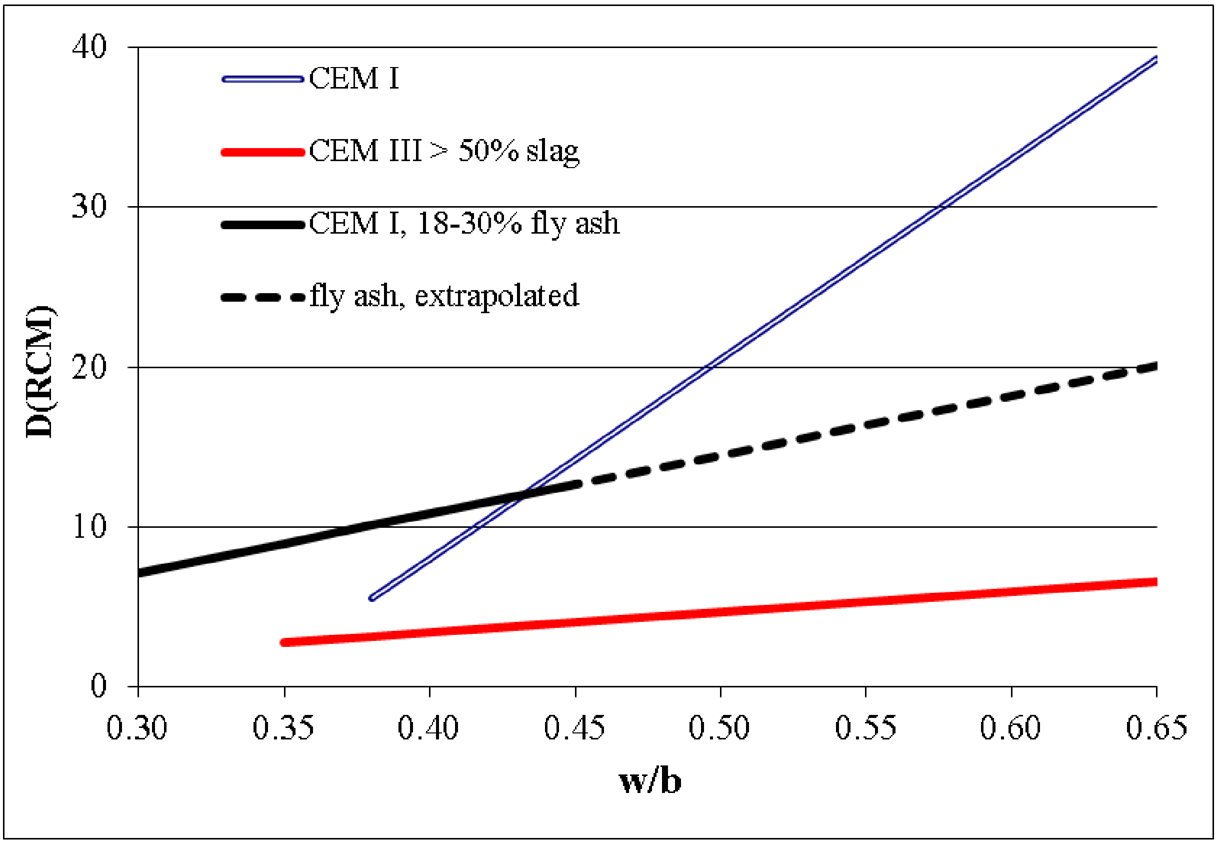

*Figure 3 Dependency of chloride migration coefficient on w/b [25, 26]*

From further analysis of the database, the time dependency of migration coefficients was shown to depend on the binder type. For ages between 28 days and three years, migration coefficients showed exponential decrease with a high exponent for fly ash binder; an intermediate value for slag binder and a relatively low exponent for Portland cement. Similar results were found by [5, 28].

A concern for slag cement may be its relatively slow early hydration, as a more porous microstructure at early age may be a disadvantage when the concrete is exposed to chloride at earlier ages than 28 days, as is usually assumed. Recent work has clarified this issue: it appears that up to seven days the diffusion coefficient for chloride in slag cement mortar is higher than for Portland cement mortar, but from then on progressively becomes much lower as shown in Figure 4. Modelling has shown that the effect of exposure to chloride at one day age compared to 28 days for a total exposure period of 50 years is very small [29]. Over 50 years, chloride penetration is much lower for slag cement than for Portland cement in a comparable situation.

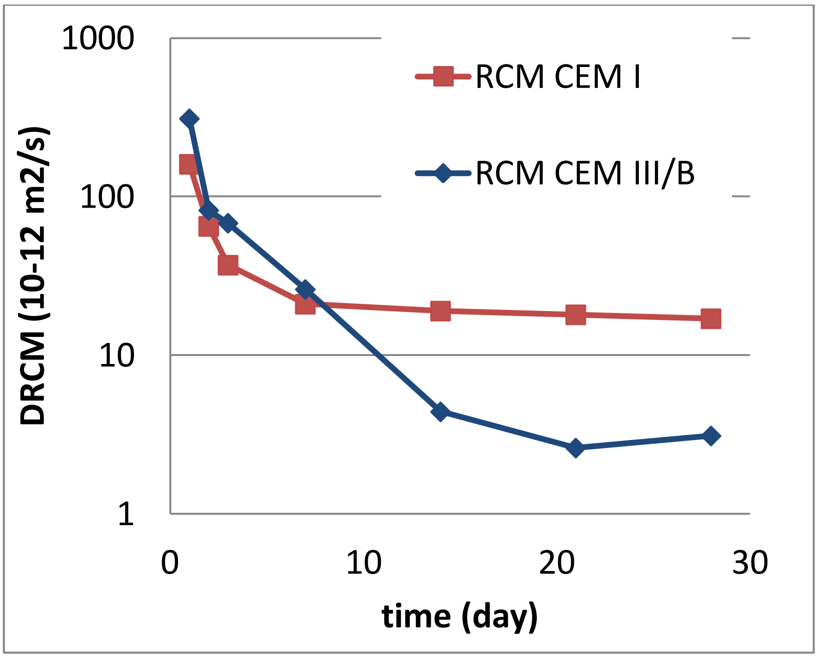

*Figure 4 Chloride migration coefficient for Portland and slag cement mortar between one and 28 days age; note: Y-axis log scale [29]*

With service life modelling as the objective, questions regarding the critical chloride content arose. The case for slag concrete has not been clarified completely, but present limited information suggests that critical chloride levels in slag cement concrete are similar to those in Portland cement concrete [30, 31]. In the experiments with salt/drying exposure described above [14], steel potentials were used to determine initiation of corrosion. Plotting the probability of corrosion against the chloride content at the depth of the steel bars showed that the critical chloride content depended most strongly on w/b and did not significantly depend on binder type. It was also observed that the corrosion rate of steel bars, after corrosion had initiated and with similar chloride contents, was lower in blended cement concrete than in Portland cement concrete. A relative weakness of slag cement is its higher sensitivity to poor curing [32].

## 3. FLY ASH RESEARCH RELATED TO CHLORIDE PENETRATION AND CORROSION

Research on fly ash parallel to that mentioned for slag has been conducted in The Netherlands since the 1990s. For typical fly ash replacement levels of about 27% in CEM II/B-V, high resistivities, see Figure 2, and low corrosion rates were found [14]. Chloride diffusion may be relatively high at 28 days, but progressively becomes much lower over say up to one year, approaching that of slag cement. Fly ash hydration is apparently slower than slag hydration, requiring up to several months to fully develop its beneficial effects, including high resistivity [14, 18]. Fly ash diffusion coefficient dependency on w/b (note: counting all fly ash as binder) is intermediate between slag and Portland cement [25, 26] as shown in Figure 3. A recent study exploring extremely low clinker contents showed that with 250 kg “binder” per cubic meter with 30 to 70% fly ash of total binder, relatively low diffusion coefficients could be obtained at one year age [33]. Such concretes, however, are very sensitive to poor curing, as they carbonate rather quickly and show increased freeze-thaw damage if not hydrated properly, that is, by long wet curing.

Although studied much less, Dutch work on “ternary” blends of slag and fly ash and of fly ash and silica fume may provide additional data. Concretes made with so-called composite cements, CEM V/A (S-V), containing c. 25% slag and c. 25% fly ash, were found to produce low chloride migration coefficients and high resistivity, see Figures 1 and 2 [14, 18]. In the 1990s a mix with 10% fly ash and 5% silica fume was studied for chloride diffusion (by immersion) and resistivity: it produced low diffusion and high resistivity values [12, 34]. It approached the behaviour of classic slag cement concrete. In these respects, it performed particularly better than a mix with 5% silica fume (to Portland cement) only.

## 4. SUMMARY AND CONCLUSIONS

Studies of concrete in the field in marine environment on structures up to 60 years of age and several decades of laboratory work have shown that concrete made with cement that contains about 70% of blast furnace slag (nowadays termed CEM III/B LH SR) shows excellent behaviour with respect to chloride penetration and reinforcement corrosion. In comparative studies it was observed that chloride penetration in Portland cement concrete was deeper and faster. Chloride profile analysis revealed that chloride surface contents were similar, but diffusion coefficients were consistently lower for slag cement than for Portland cement. The decrease over time of apparent diffusion coefficients in slag cement is stronger than in Portland cement concrete. Slag cement concrete has a higher electrical resistivity and lower corrosion rate after depassivation. Slag cement hydration is slower than Portland clinker hydration, but from about seven days age on chloride migration is slower in the former than in the latter. Similarly, cement with moderate fly ash replacement of Portland clinker shows lower diffusion coefficients and higher resistivities than Portland cement, in particular after a few months of hydration. Composite cements with slag and fly ash at about 50% clinker replacement behave similarly. Critical (corrosion initiating) chloride contents appear comparable for all cement types mentioned. Summarising, replacement of clinker by slag at high levels (50 – 70%) and fly ash at intermediate levels (20 – 30%) produces high chloride penetration resistance and high electrical resistivity, overall decreasing the risk of corrosion in chloride contaminated environments. The need for sufficiently long wet curing is the main concern with slag and in particular fly ash based blended binders.

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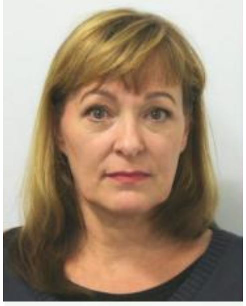
# The effect of slag and fly ash on interaction of chloride penetration and carbonation



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## ABSTRACT

This paper summarizes a study on the effect of concrete carbonation on chloride penetration and the effect of chlorides on carbonation, both also with added fly ash (FA) or blast furnace slag (BFS). Chloride migration was always more with carbonation, and especially when FA or BFS was included. However it must be noted that chloride migration was lower both with and without carbonation for the mortars with FA or BFS. Instead chlorides in concrete were found to decrease carbonation.

This was found to happen especially when the binding material was sulphate resistant cement (CEM I). The meaning of these interactions taking place only in the concrete surface layer should be understood, as well as what is the overall meaning of the binding material, and FA or BFA, on concrete service life.

**Key words:** chlorides, carbonation, interaction, combined deterioration, durability, fly ash, blast furnace slag.

# 1. INTRODUCTION

## 1.1 Background

Recently, the corrosion of concrete structures has received great attention related with the deterioration of sea-side structures, such as new airports, bridges, and nuclear power plants. In this regard, many studies have been done on chloride attack in concrete structures. However, those studies are confined mostly to single deterioration due to chloride only, although actual environment is rather of combined type including also e.g. carbonation. However there are also some studies dealing with the effect of pozzolans on chloride penetration combined with carbonation. [1 – 4] At the same time the effect of carbonation and drying on concrete pore structure, also including the effect of fly ash (FA) and blast furnace slag (BFS), has already been studied for a long time.

For instance in [1] it was found that the diffusion resistance of pastes with OPC, OPC/30% FA and OPC/65% BFS were all adversely affected by both drying (RH 65 %) and carbonation. This was associated with coarsening of the pore structure. The effects were more severe for FA- and BFS-blended cements than for OPC.

According to [4], exposure to carbon dioxide significantly decreases the chloride penetration resistance of mortar containing pozzolans. This decrease is related to the replacement level of pozzolans. The incorporation of pozzolans reduces the calcium hydroxide and the pH level of mortar. The exposure to carbon dioxide further reduces this and renders the mortar susceptible to chloride attack. Based on the results in [4] the high level of replacement by a pozzolan, therefore lowers the resistance to chloride penetration.

According to an analysis presented in [2], BFS-concrete shows the longest expected service life if only individual chloride exposure is considered. However, significant decreasing of service life of BFS-concrete was realized after cyclic exposure was considered (by a Japanese (JSCE) simulation method). Releasing of fixed chloride due to carbonation of BFS-concrete is expected to increase the concentration of free chloride in pore solution. Then there is a larger concentration gradient forcing chlorides to penetrate deeper inside the concrete. A larger carbonation depth of BFS-concrete, compared to PC-concrete, causes a larger chloride content diffused into the concrete.

On the other hand, penetration of chlorides into a deeper region, i.e. into non-carbonated concrete, can be expected to decrease with the use of BFS. This was also found in [3] in the case of concretes with FA, and is because of finer pore structure and higher binding capacity. The effect of combined environment with both carbonation and chloride attack (cyclic exposure) was considered by studying both concretes with FA and without FA. Based on these results it was concluded that though the use of FA pronounces the chloride ion concentration of the surface, the amounts of chloride ion penetration into deep regions decreases with the use of FA. In all, the overall long term effect of combined carbonation-chloride exposure must be based on studies and modelling considering all the aspects. These include first of all the type of combined carbonation-chloride exposure. And after that the effect of carbonation and drying on concrete pore structure, the effect of the release of chlorides by carbonation on chloride penetration at concrete near the surface region and further diffusion of chlorides into deeper regions with no carbonation.

### 1.2. Finnish DuraInt research project

The experimental study addressed here on with the chloride-carbonation interactions was included in a more comprehensive Finnish research project called DuraInt (*Deterioration Parameters on Service Life of Concrete Structures in Cold Environments, 2008 - 2011*). It was undertaken by VTT Technical Research Centre of Finland in cooperation with the Department of Civil and Structural Engineering at the University of Aalto. The overall objective of the project was to evaluate the effect of interacted deterioration parameters on the service life of concrete structures.

It was expected that coupled deterioration is different for concretes with different binding materials. That is why concretes with added BFS or FA were also included as well as cements mixed with some BFS (CEM II/A-M(S-LL) 42,5 N). BFS and FA were also included because they are used in Finland as additions when appropriate, e.g. to diminish hydration heat development, as well as to facilitate sustainable construction. A desired service life closely linked with sustainability is always considered in the first place, and especially in aggressive environments including both carbonation and salt exposure.

All laboratory tests in the DuraInt project were designed to investigate the coupled interaction of deterioration mechanisms. This included evaluation of internal damage due to frost, scaling due to frost-salt attack, chloride ingress, and carbonation. The laboratory testing program was divided into five parts with different interactions. When reasonable, these interactions were cross-studied. [5] One project task addressing service life modelling created ways to model interacted deterioration based on laboratory and field results. [6, 7]

## 2 EXPERIMENTAL

### 2.1 Materials

Three different Finnish cements as well as BFS manufactured by Finnsementti Oy, and fly ash (FA) were used. The basic information on the binding materials is presented in Table 1, as well as information on the used admixtures. The chemical composition of the binding materials can be found in [8].The content of $C_3A$ for CEM I was 2 %, and for both CEM II cements it was 8,5 %. Granitic aggregate with maximum aggregate sizes of either 16 mm (concretes) or 2 mm (mortars) was used.

*Table 1 – Basic information on cements, additives and admixtures.*

| Product Name | Cement/Additive/Admixture | Type | Setting time at +20 C [min] | Blaine fineness [m$^2$/kg] | Strength [MPa] |  | BFS [%] | FA [%] | Lime-stone [%] |
|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  | 1 d | 28 d |  |  |  |
| SR-sementti (Lappeenranta) | CEM I 42,5 N - SR | Normally hardening sulphate resistant portland cement | 200 | 330 | 13 | 54 | 0 | 0 | 1 |
| Rapid sementti (Parainen) | CEM II/A-LL 42,5 R | Early strength blended cement | 160 | 440 | 22 | 54 | 1 | 0 | 6 |
| Yleissementti (Parainen) | CEM II/A-M(S-LL) 42,5 N | Normally hardening blended cement | 170 | 380 | 14 | 49 | 7 | 0 | 6 |
| Masuunikuonajauhe (BFS) ”KJ400” | BFS | Blst furnace slag (Specific gravity 2980 kg/m$^3$) | - | 400 | - | - | 100 | 0 | 0 |
| Fly ash | FA | Fly ash [EN 450-1. 2005] Fineness N, Class A (Specific gravity 2200 kg/m$^3$) | - | ca. 250 | - | - | 0 | 0 | 0 |
| Glenium G 51 | Superplasticizer [EN 934-2] | Modified polycarboxylic ether (PCE) | - | - | - | - | - | - | - |
| Ilma-Parmix | Air-entraining agent [EN 934-2] | Fatty Acid Soap | - | - | - | - | - | - | - |

## 2.2 Test methods

Both the effect of carbonation on chloride migration (Cl-migration), and the effect of chlorides in concrete on carbonation were studied. A study on the effect of carbonation on chloride release, including the effect of this on further chloride penetration was also initiated.

The first test series (TS 1) was with concretes. The effect of carbonated concrete on chloride migration was studied using the ´NT Build 492´ method [9]. This was done by having a carbonated middle part (ca. 18 mm; h50 mm) in the specimens (Ø98 mm; h50 mm) for Cl-migration testing (two carbonated surfaces were glued together before coring of the specimen). Accelerated carbonation was at 4 % $CO_2$ (RH 60 %). The reference was the non-carbonated part of the specimen (sides). Testing was at 4.9 months age. Chloride penetration was made visible with silver nitrate, $AgNO_3$. The TS 1 testing procedure is presented in Figure 1.

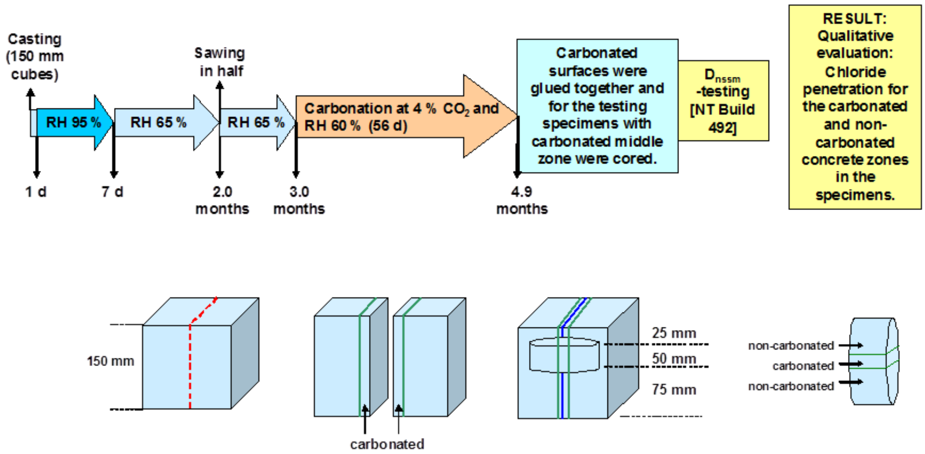

*Figure 1 - Testing series TS 1; testing with concrete. Procedure for interacted carbonation and chloride penetration. [5]*

The second test series (TS 2) was done with mortars. Specimen (Ø98 mm; h50mm) including a carbonated surface layer were used to study the effect of carbonation on Cl-migration. The carbonated specimen side was the Cl-side in the migration testing. Carbonation before Cl-migration testing was at RH 65 % for 2 months, and after that at 4 % $CO_2$ (5.2 months). The reference testing was with non-carbonated specimen. The procedure for this interacted carbonation and chloride penetration testing for mortar is shown in Figure 2.

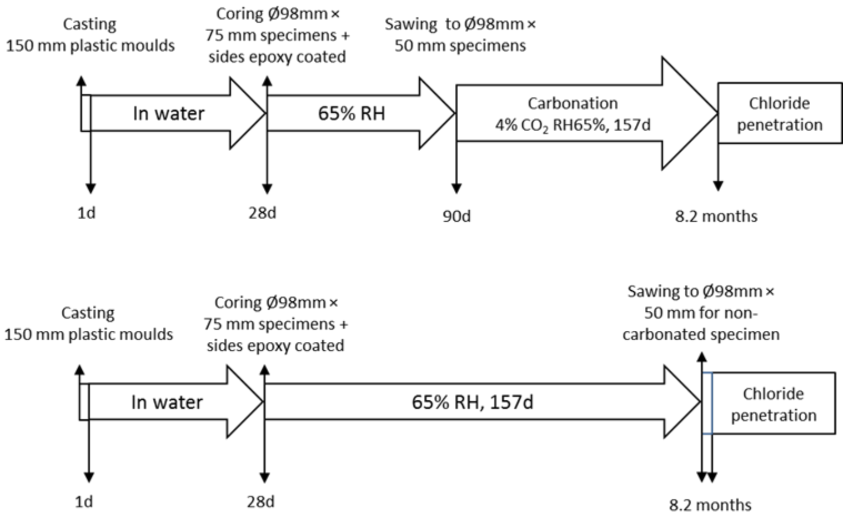

*Figure 2 – Testing series TS 2; testing with mortars. Procedure for interacted carbonation and chloride penetration. [5]*

The third test series (TS 3) was with the same concretes as test series TS 1. The effect of chloride penetration on carbonation was studied. The testing procedure is presented schematically in Figure 3. Chloride penetration was first using the test setup of accelerated chloride migration [9]. After that there was additional drying at RH 65 % for 1.8 months (weight change < 0.2 % per day), and finally accelerated carbonation at 4 % $CO_2$ (RH 60 %) for 56 d. The reference specimens were the same chloride migration specimens but in that case carbonation was measured from the NaOH-side, i.e. there were no chlorides in concrete, and thus the result was carbonation without chlorides.

To get additional reference data in TS 3, i.e. carbonation depth without chlorides, and also without any Cl-testing, half concrete cubes ($75 \times 150 \times 150$ $mm^3$) were used. The casted cubes were sawed horizontally in half at the age of 2 months and the halves were placed to a laboratory climatic room with relative humidity of 65% and temperature +20°C. At the age of three months these halved cubes were placed to a carbonation chamber (4% $CO_2$ and RH 65 %) for 56 days. Carbonation depth of the sawed concrete surface was determined principally according to [10].

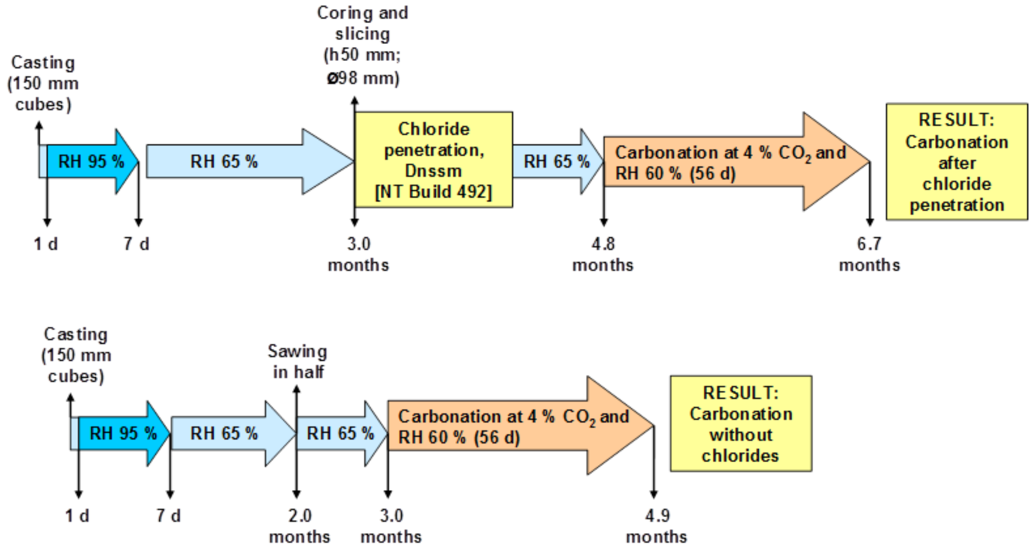

*Figure 3 – Testing series TS 3; testing with concrete. Procedures for effect of chloride penetration on concrete carbonation, and carbonation of reference concrete without chlorides.*

## 2.3 Mixes

In all testing series, the calculation of the effective water-binder ratio (w/b) the amount of BFS was taken as multiplied by 0.80 and FA was taken as multiplied by 0.40 (w/b = $W_{eff}$/(Cement + 0.80×BFS + 0.40×FA).

Composition information and compressive strength for the mixes in all three testing series is presented in Table 2.

*Table 2 – Concrete and mortar composition and compressive strength.*

| Testing series | Short code | Binding materials | w/b = Weff/(Cement + 0.80×BFS + 0.40×FA) | Binding materials [kg/m$^3$] | | | Total effective water [kg/m$^3$] | Aggregates [kg/m$^3$] | Air content (fresh concrete) [%] | Compressive strength [MPa] | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Cement | BFS | FA | | | | 7d | 28d |
| TS 1 & TS 3 (Concretes) | SR05A2 | CEM I 42.5 N | 0,50 | 321 | 0 | 0 | 160 | 1965 | 2 | 45,8 | 62,7 |
| | Y05A2 | CEM II/A-M(S-LL) 42.5 N | 0,51 | 333 | 0 | 0 | 170 | 1899 | 1,4 | 42,8 | 57,4 |
| | Y05A5 | CEM II/A-M(S-LL) 42.5 N | 0,51 | 333 | 0 | 0 | 170 | 1844 | 4,4 | 36,9 | 50,8 |
| | R-BFS05A2 | CEM II/A-LL 42.5 R & BFS | 0,50 | 240 | 120 | 0 | 168 | 1888 | 2,2 | 43,5 | 66,8 |
| | R-FA05A2 | CEM II/A-LL 42.5 R & FA | 0,50 | 300 | 0 | 72 | 165 | 1885 | 2,5 | 47,1 | 64,9 |
| TS 2 (Mortars) | M-Y05A2 | CEM II/A-M(S-LL) 42.5 N | 0,50 | 576 | 0 | 0 | 290 | 1315 | 4,1 | - | 43,2 |
| | M-Y-BFS05A | CEM II/A-M(S-LL) 42.5 N & BFS | 0,49 | 440 | 220 | 0 | 299 | 1226 | 3,4 | - | 52,3 |
| | M-Y-FA05A2 | CEM II/A-M(S-LL) 42.5 N & FA | 0,51 | 542 | 0 | 130 | 304 | 1193 | 4,6 | - | 45,5 |

## 2.4 Results and discussion

*Testing series TS 1*

In testing series TS 1 the result was not quite clear as there were difficulties to define the penetration depth of chlorides in the carbonated concrete. This was because of too narrow carbonated middle zone, and too big aggregate grains compared with the width of the zone. However, it could be found out that at least in the case of FA-concrete (concrete RFA05A2 with CEM II/A-LL 42,5 R and FA) that carbonation clearly increased chloride penetration. Examples on the split specimen surfaces after silver nitrate treatment for FA-concrete are presented in

Figure 4. The same kind of figures for all the other concretes can be found in DuraInt project report [5]. For the other concretes the result was even more unclear than for FA-concrete. After this more or less unclear result in TS 1 additional testing was done with mortars, and in this case with the carbonated surface layer in the chloride migration testing (TS 2).

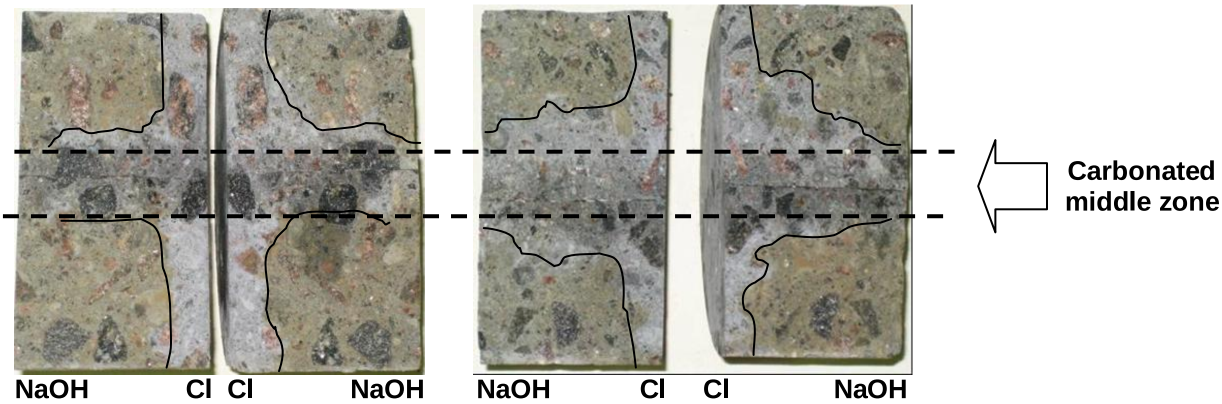

*Figure 4 - Concrete R-FA05A2. Split specimen surfaces after chloride migration testing [9]. Silver nitrate indicator has been sprayed on the surfaces to detect chlorides.*

*Testing series TS 2*

The results for the testing series TS 2 are presented in Table 3. It must be noted that the used voltages and testing times were not the same for different mortars, and thus for also for different binding materials. This means that the chloride penetration depths for different mortars cannot be directly compared despite having used the same test setup for the same concrete with and without carbonated surface layer.

It was found that chloride penetration was more, and $D_{nssm}$ was higher for the specimen with carbonated surface layer, compared with the specimen with no carbonation. The relative increase was more for mixes with added BFS and FA. This effect was clearer for the mortar with FA. However it must be noted that $D_{nssm}$ was still lower both with and without carbonation for the mortars with FA or BFS, compared with the mortar with only CEM II/A-M(S-LL) 42,5 N.

*Table 3 – TS 2. The effect of carbonation on Cl-penetration and non-steady state migration coefficient ($D_{nssm}$).*

| | RCM test setup | | With carbonated surface layer | | | No carbonation | |
|---|---|---|---|---|---|---|---|
| **Mortar** | **Applied voltage** | **Test duration** | **Carbonation** | **Chloride penetration** | **$D_{nssm}$** | **Chloride penetration** | **$D_{nssn}$** |
| | **[VDC]** | **[h]** | **[mm]** | **[mm]** | **[$\times10^{-12}$ $m^2/s$]** | **[mm]** | **[$\times10^{-12}$ $m^2/s$]** |
| **M-Y05A2** | **30** | **3,5** | **8,1** | **12,3** | **37,6** | **8,5** | **24,8** |
| **M-Y-BFS05A2** | **60** | **10,0** | **4,9** | **11,2** | **6,2** | **7,4** | **3,9** |
| **M-Y-FA05A2** | **60** | **6,0** | **8,4** | **12,7** | **11,8** | **3,8** | **3,1** |

*Testing series TS 3*

The results for the testing series TS 3 are presented in Table 4 and in Figure 5. The carbonation with chlorides was 3 % - 80 % of the carbonation without chlorides. With CEM I 42,5 N - SR carbonation was minimal when there was first accelerated Cl-migration testing and carbonation after that. The reason for this can be higher concrete moisture content due to chloride hygroscopy, thus decreasing the carbonation rate[11]. Pores may also become blocked as a result of the salt crystallization in the pores network. Concrete with CEM I 42.5 N – SR has low chloride binding capacity and this may be the reason for the minimal carbonation when chlorides were introduced before carbonation. The lowest effect of chlorides was for the concrete with air entrainment (Y05A5). This may also be because of the less accurate measurement of the carbonation depth which was also affected by the air pores, as could be seen also based on the fluctuating carbonation front in the specimens.

There were no big differences between the concrete with CEM II/A-M(S-LL) 42,5, and the concretes with CEM II/A-LL 42,5 and BFS or FA (Figure 5).

The cementitious matrix may undergo certain alterations in conditions of the combined effects of cement hydration, chloride ion transport and chemical binding mechanics. It is difficult to know which are the most relevant reasons in this study for the lower carbonation with chlorides.

*Table 4 – TS 3. Chloride penetration after chloride migration testing, and carbonation of the same specimens with and without Cl-penetration (Cl- and NaOH-sides), and carbonation without any migration testing (additional half cubes). Carbonation in all cases at 4 % $CO_2$ (RH 60 %).*

| Concrete | Chloride penetration before carbonation [mm] | Chloride side - Carbonation [mm] 1) | | Sodium hydroxide side - Carbonation [mm] 1) | | Half cubes without Cloride migration testing | |
|---|---|---|---|---|---|---|---|
| | | Carbonation at 56 d [mm] | Standard deviation [mm] | Carbonation at 56 d [mm] | Standard deviation [mm] | Carbonation at 56 d | Standard deviation [mm] |
| **SR05A2** | **30,0** | **0,2** | **0,0** | **7,3** | **1,1** | **7,5** | **0,7** |
| **Y05A2** | **32,0** | **4,4** | **0,6** | **6,8** | **0,6** | **9,5** | **0,7** |
| **Y05A5** | **30,0** | **8,6** | **2,0** | **10,8** | **0,5** | **10,7** | **0,7** |
| **R-BFS05A2** | **13,0** | **4,2** | **1,1** | **6,8** | **1,4** | **7,0** | **0,8** |
| **R-FA05A2** | **>12** | **4,3** | **0,7** | **8,0** | **1,0** | **10,2** | **0,9** |

1) 2 specimens (ø98 mm)/concrete. Carbonation from the sawed surface. In all 8 - 11 measurement points/concrete

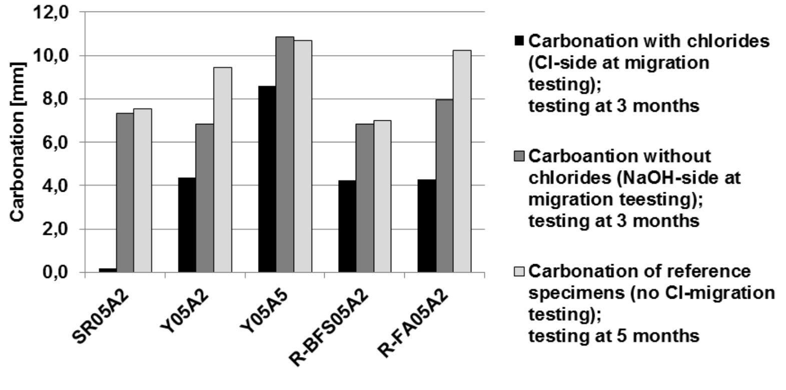

*Figure 5 - Effect of chlorides on carbonation. Carbonation depths after 56 d at 4 % $CO_2$.*

## 3 CONCLUSIONS

This experimental study dealing with the chloride-carbonation interactions was included in a more comprehensive Finnish DurtaInt research project (Deterioration Parameters on Service Life of Concrete Structures in Cold Environments, 2008 - 2011). In this project it was found that single attacks tested in laboratory conditions yield different results than what may actually be experienced in field applications or in-situ concrete structures, where multiple degradation types are occurring simultaneously.

The overall long term effect of combined carbonation-chloride exposure should be based on studies and modelled considering first of all the type of combined exposure. The effect is presumably irrelevant if carbonation is minimal because of e.g. constantly high concrete moisture content. When also drying of concrete is included, combined carbonation-chloride interaction may have some effect on the predicted service life. In most cases chloride penetration can be expected to be decisive. Here it was found that surface carbonation increased chloride migration as tested by ´NT Build 492´ method [9]. The relative increase was more with added FA or BFS, but still the chloride migration coefficient was in all cases much lower with added FA or BFS. On the other hand when there were chlorides in concrete carbonation always decreased. This decrease was found to be significant with CEM I 42,5 N - SR. For all the other mixes chlorides also degreased carbonation but the degrease was moderate, and there were no big differences between the mixes with cement CEM II/A – M(S-LL) 42,5 N (including 6 % BFS), and the mixes with CEM II/A-LL 42,5 R (1 % BFS) including also separately added FA (24 % of cement) or BFS (50 % of cement). The releasing of fixed chlorides due to carbonation is expected to increase the concentration of free chloride in the pore solution and as a consequence also the chloride penetration deeper into the concrete. No results on this are included here.

There are several reasons behind the detected carbonation-chloride interactions. These include the effect of carbonation and drying on concrete pore structure, concrete permeability and diffusion properties, and also the effect of the release of chlorides by carbonation. In all these effects the binding material and the amount of FA or BFS will have a definite impact. As most interacted deterioration takes place mainly in the concrete near the surface layer, the meaning of this must be understood.

The Finnish DuraInt project did not include any exhaustive studies on all of the aspects and reasons behind the found coupled interaction of deterioration mechanisms, as carbonation-chloride interaction. Further studies should include more profound studies to better understand the interaction aspects and their meaning for assessing the service life of concrete structures. Concretes with different kind of binding materials, including FA and BFA, should be studied, as well as the impact of different kinds of natural exposures.

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# Blast Furnace Slag for Durable Concrete Infrastructure in Marine Environments

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## ABSTRACT

For important concrete infrastructures in marine environments it should always be very important to apply a concrete with a highest possible resistance against chloride penetration. If the risk for early-age exposure during concrete construction is high, a high early-age resistance against chloride penetration should also be very important. For severe marine environments, the documentation as outlined and discussed in the present paper shows that concrete with a binder system based on granulated blast furnace slag would give a much better durability compared to that of other types of binder system.

**Key words:** Concrete infrastructure, marine environments, chloride penetration, rebar corrosion, binder system, blast furnace slag, chloride diffusivity, early-age exposure, low curing temperature.

## 1. INTRODUCTION

Although a number of different deteriorating processes may affect the durability and service life of concrete structures in marine environments, extensive experience demonstrates that it is not the disintegration of the concrete itself but rather chloride-induced corrosion of embedded steel which poses the most critical and greatest threat to the durability and long-term performance of concrete structures in such environments [1]. After a comprehensive surveying of concrete structures in U.S. waters, the problem with corrosion of embedded steel was pointed out by Wig and Ferguson [2] already in 1917. Also in Norwegian marine environments, chloride-induced corrosion of embedded steel has been the major threat and problem to the operation and safety of a large number of important concrete structures, the first of which was produced in 1910 [1,3-5].

Along the Norwegian coastline there are more than 10,000 harbour structures, most of which are concrete structures which have typically started to corrode within a period of 10 years. Also, there are more than 300 large concrete coastal bridges built after 1970, of which more than 50%

are corroding, one of which was so heavily corroded after 25 years that it had to be demolished. Since 1970, 34 offshore concrete structures for the North Sea with a superior durability compared to all the other concrete structures in Norwegian waters have been produced. Also for these offshore structures, however, penetration of chlorides has caused corrosion damage, only at a slower rate and lower extent.

For all the above concrete structures produced since 1970, the question may be raised why so much stricter durability requirements for all the offshore concrete structures were specified [6], compared to that for all the other important concrete infrastructures produced along the Norwegian coastline during the same period. At the same time, a service life of only 30 to 60 years for all the offshore structures was typically specified, while for all the land based concrete structures, the specified service life was typically 60 to 100 years. For all the offshore concrete structures, a much stricter concrete quality control during concrete construction was also specified. In spite of this, also the offshore concrete structures got a high scatter and variability of achieved construction quality, and it is mostly the local weaknesses in these structures which have contributed to much of the very costly repairs carried out later on [1]. Also for all the offshore concrete structures, it should be noted that only prescriptive durability requirements were specified, which could not be verified and controlled for proper quality assurance during concrete construction.

Although the resistance of the concrete against chloride penetration to a great extent is controlled by the specification of a low water/binder ratio, extensive documentation in the literature demonstrates that the selection of a proper binder system may be more important than the specification of a low water/binder ratio. For almost all the above concrete structures in Norwegian waters, it should be noted that the structures have typically been produced with concrete based on pure portland cements, although a binder system based on blast furnace slag would have given a superior resistance against chloride penetration. Since the first blast furnace slag cements were introduced on the market in 1888, extensive field experience and research in many countries have demonstrated that blast furnace slag cements give a much higher resistance against chloride penetration and durability compared to that of pure portland cements [7]. In countries such as The Netherlands, where blast furnace slag cements have had a high market share for a very long time, such cements have typically been applied to all marine concrete construction. As a result, very durable concrete structures for the marine environment have been obtained [7].

For all the above concrete structures in Norwegian waters, it should also be noted that the environmental conditions are very severe. For certain periods of the year, all these structures are heavily exposed to the most severe combination of wave action and splashing of seawater. For much of the concrete construction work in Norwegian marine environments, the construction also takes place all year around. Therefore, the risk for early-age exposure during concrete construction before the concrete has gained sufficient maturity and density is also very high. Thus, for several of the above concrete structures along the Norwegian coastline, a deep chloride penetration took place already during concrete construction [1].

In order to also get some experience with binder systems based on blast furnace slag in Norwegian marine environments, some experimental investigations have been carried out in recent years, a brief outline and discussion of which are given in the following. These investigations were primarily focused on the effect of early-age exposure and low curing temperature on the resistance against chloride penetration. Partly based on this documentation, a high volume slag cement was selected for the production of a number of concrete substructures for the new city development on Tjuvholmen in the harbor region of Oslo City [8]. For all these concrete structures which were produced during 2005 to 2010, a 300-year service life was required, which means that the structures should be produced with a highest possible durability and long-term performance. For the high volume slag concrete applied to all these concrete structures, an extensive documentation of the frost resistance of the concrete was also carried out, the results of which is also briefly outlined and discussed in the following.

## 2. CHLORIDE PENETRATION

### 2.1 General

For concrete structures in chloride containing environments, the penetration of chlorides can take place in different ways. Through un-cracked concrete, the penetration mainly takes place by capillary absorption and diffusion. When a relatively dry concrete is exposed to saltwater, the concrete will suck the saltwater relatively fast, and intermittent wetting and drying can successively accumulate high concentrations of salt in the concrete. For concrete structures in moist marine environment, however, intermittent exposure to splashing of seawater mainly gives fluctuating moisture contents limited to an outer layer of the concrete. For conditions along the North Sea coasts, the moisture content only shows small fluctuations in the outer layer of the concrete, while it appears to be more constantly high deeper in below the concrete surface (Figure 1). For many concrete structures in Norwegian waters, however, constantly high moisture contents have typically also been observed in the outer layer of the concrete. For concrete coastal bridges along the Norwegian coastline, a degree of capillary saturation typically varying from 80 to 90% in the outer 40 to 50 mm of the concrete has been reported [10]. For the thickness of concrete cover typically being specified for concrete structures in chloride containing environments, the moisture content in the concrete may be quite high, and hence, diffusion appears to be a most dominating transport mechanism for the penetration of chlorides.

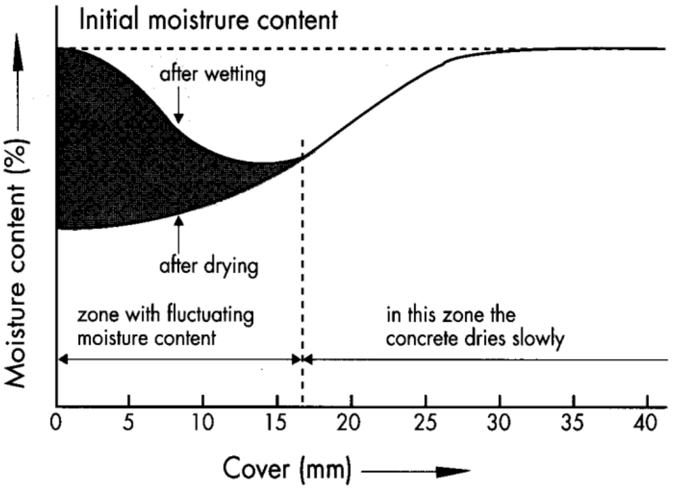

*Figure 1 – Outer layer of the concrete with changing moisture content under splash water conditions along the North Sea coast [9].*

Although penetration of chlorides into concrete has been the subject to extensive research both from a theoretical and applied point of view, it still appears to be a very complex and difficult issue [11]. Even pure diffusion of chloride ions into concrete is a very complex transport process [12]. Therefore, when Fick´s 2. Law of Diffusion is often applied for calculation of chloride penetration rates into concrete, it should be noted that such a calculation is based on a number of assumptions and a very rough simplification of the real transport mechanism.

For a general evaluation of the resistance of concrete against chloride penetration, a number of factors have to be considered. Although the water/binder ratio of the concrete is a most important controlling factor, it is well documented in the literature that the selection of a proper cement or binder system may be more important than the selection of a low water/binder ratio. For example, when the water/binder ratio was reduced from 0.50 to 0.40 for a concrete based on pure portland cement, the chloride diffusivity was reduced by a factor of 2 to 3, while incorporation of various types of supplementary cementitious materials such as blast furnace slag, fly ash or silica fume at the same water/binder ratio reduced the chloride diffusivity by a factor by up to 20 [13]. While a reduced water/binder ratio from 0.45 to 0.35 for a concrete based on pure portland cement may only reduce the chloride diffusivity by a factor of 2, a replacement of the portland cement by a blast furnace slag cement may reduce the chloride diffusivity by a factor of up to 50 [7]. By also combining the blast furnace slag cement with silica fume at very low water/binder ratios, very low chloride diffusivities can be obtained and hence, concretes with a very high resistance against chloride penetration can be produced [1].

## 2.2 Effect of cement type

Figure 2 shows the resistance against chloride penetration of four different types of commercial cement produced with the same concrete composition at a water/binder ratio of 0.45. These cements include two blast furnace slag cements of type CEM II/B-S 42.5 R NA with approximately 34% slag (GGBS1) and type CEM III/B 42.5 LH HS (GGBS2) with approximately 70% slag, respectively, one high performance portland cement of type CEM I 52.5 LA (HPC) and one fly ash cement of type CEM II/A V 42.5 R with approximately 20% fly ash (PFA). The resistance against chloride penetration was determined on the basis of chloride diffusivity tested by use of the Rapid Chloride Migration (RCM) method [15]. All testing was carried out on water cured concrete specimens at $20^0$C for periods of up to 180 days. In order to compare the same types of cement in a more dense concrete, the same cements were also tested in combination with 10% silica fume by weight of cement at a water/binder ratio of 0.38 (Figure 3).

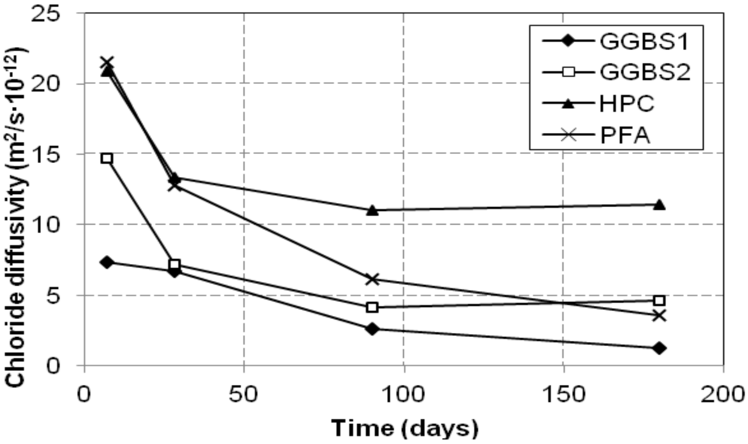

*Figure 2 – Effect of cement type on the resistance of concrete against chloride penetration at a water/binder ratio of 0.45 [14].*

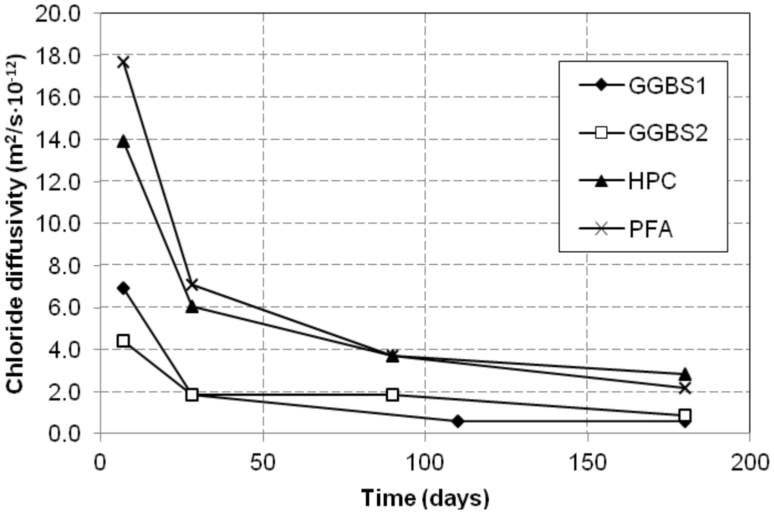

*Figure 3 – Effect of cement type on the resistance of concrete against chloride penetration at a water/binder ratio of 0.38 [14].*

The results in Figures 2 and 3 demonstrate that the two slag cements gave a distinctly higher resistance against chloride penetration compared to that of the fly ash cement and a substantially higher resistance compared to that of the portland cement. In the more dense concrete with silica fume, the difference between the different types of cement was smaller than in the more porous type of concrete. However, even in the densest concrete, it was still a distinct difference between the two slag cements and the other cements. Also, both types of slag cement showed a very high early-age resistance compared to that of the other types of cement, and this may be very important for early-age exposure during concrete construction in severe marine environments.

In order to also test the effect of low curing temperature, the same types of cement were tested at curing temperatures of 5, 12 and $20^0$C, respectively. Since ordinary portland cements have been so widely applied for marine concrete construction in Norwegian waters, the 34% slag cement was replaced by an ordinary portland cement of type CEM I 42.5 R (OPC). Otherwise, all tests were carried out for the same concrete composition as that above with a water/binder ratio of

0.45. As can be seen from Figures 4 to 6, the 70% slag cement (GGBS2) gave a substantially higher resistance against chloride penetration than both the fly ash cement (PFA) and the two pure portland cements (HPC and OPC). Thus at $5^0$C, the 28-day chloride diffusivity for the slag cement was 7.9 x $10^{-12}$ $m^2/s$ compared to 17.4 x $10^{-12}$ $m^2/s$ for the fly ash cement (PFA) and 19.3 and 20.3 x $10^{-12}$ $m^2/s$ for the two pure portland cements (HPC and OPC), respectively. After 90 days of curing, the corresponding values were 4.1, 17.2, 17.6 and 14.5 x $10^{-12}$ $m^2/s$, respectively.

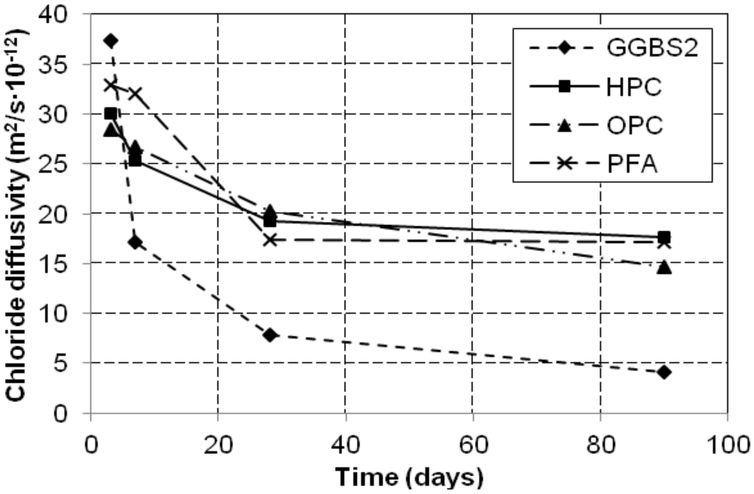

*Figure 4 – Effect of cement type on the resistance of concrete against chloride penetration at a curing temperature of $5^0$C [16].*

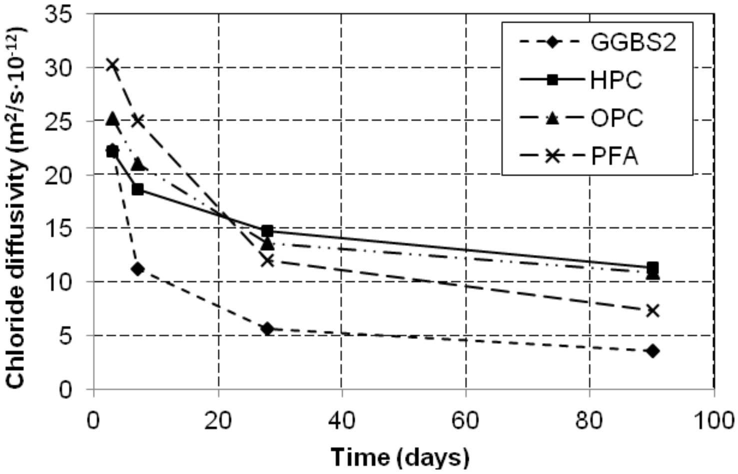

*Figure 5 – Effect of cement type on the resistance of concrete against chloride penetration at a curing temperature of $12^0$C [16].*

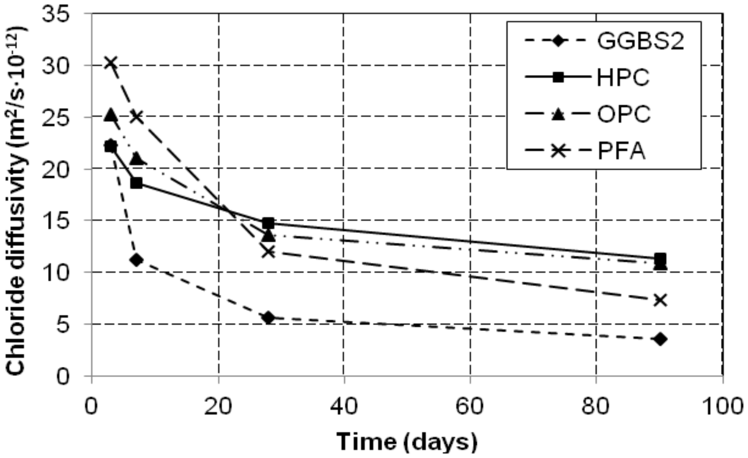

*Figure 6 – Effect of cement type on the resistance of concrete against chloride penetration at a curing temperature of 20$^0$C [16].*

Regardless of curing temperature, Figures 4 to 6 show that the slag cement gave the highest resistance, while the two portland cements gave the lowest resistance against chloride penetration for a curing period of up to 90 days. The different types of cement also showed a very different sensitivity to curing temperature. Thus, the fly ash cement was very sensitive up to the age of 90 days, while the two portland cements showed the least sensitivity to curing temperature. For severe marine environments with low curing temperatures, however, the above results clearly demonstrate that concrete structures produced with pure portland cements or fly ash cements are much more vulnerable to early-age chloride exposure compared to those produced with a binder system based on blast furnace slag.

It should be noted, that different types of portland cement may show different resistance against chloride penetration depending on the $C_3A$ content of the cement. Thus, after 100 years of exposure of large concrete units in a break water in a Japanese harbour, depths of chloride penetration of only 50 to 80 mm were observed [17]. All these concrete units had been produced with a pure portland cement with a very high $C_3A$ content of 15-16% at a water/binder ratio of approximately 0.34. For portland cements with more moderate amounts of $C_3A$, however, it appears from Figure 7 that there is only a small effect of $C_3A$ on the resistance against chloride penetration compared to that of selecting other types of binder system. The results in Figure 7 are based on field tests with concrete at a water/binder ratio of 0.50 submerged in fresh seawater at a temperature of about 7$^0$C. From the same figure, it can also be seen that the 80% slag cement confirms the superior resistance against chloride penetration compared to that of the other binder systems.

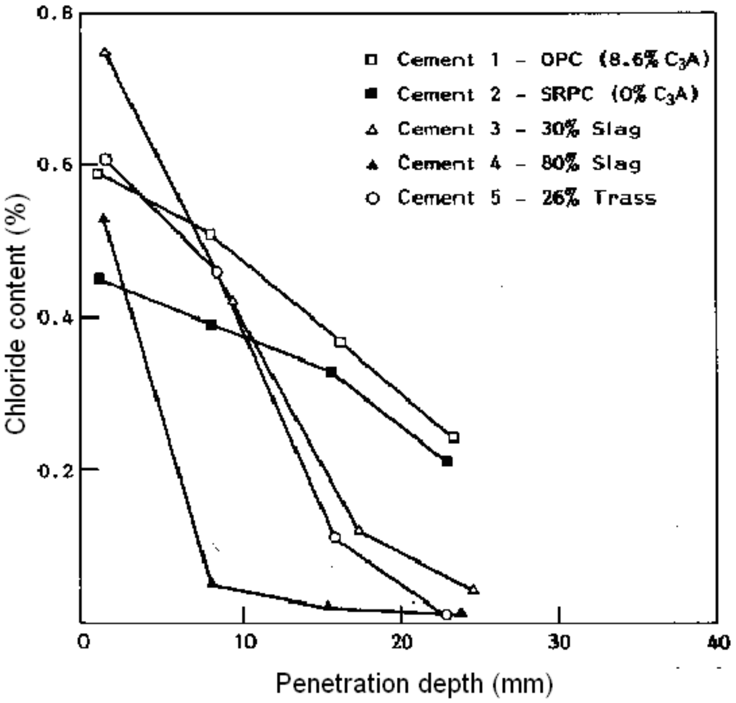

*Figure 7 – Effect of cement type on chloride penetration (by weight of cement) into concrete exposed to fresh circulating seawater [18].*

In recent years, there has been a rapid growing trend for use of more blended portland cements compared to that of pure portland cements. Replacement materials such as fly ash and blast furnace slag are often also used as separate additions to the mixture during concrete production. Then, the question is often raised on how much of the portland cement needs to be replaced in order to obtain a good resistance against chloride penetration. While blast furnace slags are hydraulic binders, most types of fly ash are pozzolanic materials, the main effect of which depends on the amount of $Ca(OH)_2$ available for the pozzolanic reaction. Thus, when the pure portland cement was replaced by more than about 30% low-calcium fly ash, it can be seen from Figure 8 that there was only a very little or no further effect on the resistance against chloride penetration. These results were based on the Rapid Chloride Permeability (RCP) method [20] on concrete with a water/binder ratio of 0.35 after one year of water curing at $20^0$C. Also, when tests with replacement of the high performance portland cement (CEM I 52,5 LA) by 20, 40 and 60% fly ash were carried out at a Norwegian construction site, it can be seen from Tables 1 and 2 that no further effect beyond about 20% replacement on the chloride diffusivity was observed. These results were based on concrete at a water/binder ratio of 0.39 after up to three years of field curing on the construction site. While the results in Table 1 were based on the RCM method [15], the results in Table 2 were based on parallel testing of the same types of concrete by use of the Immersion method [22].

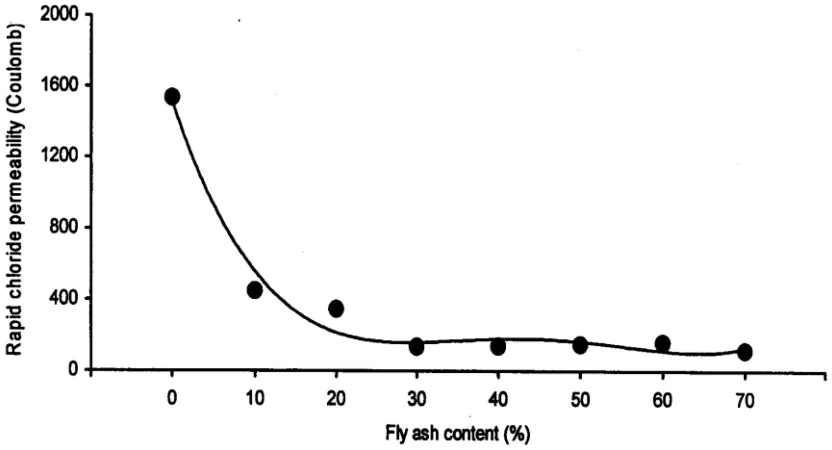

*Figure 8 – Effect of fly ash replacements on the chloride permeability (RCP) after one year of water curing at 20$^0$C. [19].*

*Table 1 – Effect of fly ash on the chloride diffusivity (RCM) after up to three years of field curing on the construction site. Mean values and standard deviation (x 10$^{-12}$ m$^2$/s) [21]*

| Concrete | 1 Year | 2 Years | 3 Years |
|---|---|---|---|
| 20% FA | 1.4<br>0.2 | 1.1<br>0.2 | 0.66<br>0.27 |
| 40% FA | 1.4<br>0.1 | 1.2<br>0.1 | 1.13<br>0.38 |
| 60% FA | 1.7<br>0.1 | 1.5<br>0.1 | 1.07<br>0.22 |

*Table 2– Effect of fly ash on the chloride diffusivity (Immersion) after two years of field curing on the construction site. Mean values and standard deviation (x 10$^{-12}$ m$^2$/s) [21]*

| | 20% FA | 40% FA | 60% FA |
|---|---|---|---|
| Chloride diffusivity | 0.48<br>0.16 | 0.44<br>0.05 | 0.50<br>0.13 |

Although portland cements can be replaced by larger amounts of blast furnace slag compared to that of fly ash, also for slag it appears to be an upper limit above which the observed effect is very small. Thus, in Figure 9, an ordinary portland cement (CEM I 42.5 R) was replaced by 40, 60 and 80% blast furnace slag with a Blaine fineness of 5,000 cm$^2$/g. Based on concrete with a water/binder ratio of 0.40 and water curing at 20$^0$ C of up to one year, the resistance of the concrete against chloride penetration was tested by use of the RCM method. After 28 days, it can be seen that increasing amounts of slag successively reduced the chloride diffusivity from 11.2 to 4.9, 3.6 and 2.3 x 10$^{-12}$ m$^2$/s, respectively, while after one year, the diffusivity of the slag concretes varied from 3.0 to 1.2 x 10$^{-12}$ m$^2$ compared to 7.0 x 10$^{-12}$ m$^2$/s for that of the pure portland cement. In parallel, a diffusion testing by use of the Immersion method [22] also showed a similar effect of the increased replacements of the portland cement by slag (Figure 10). After 28 days of water curing and further 35 days of immersion in the salt solution as required for this type of testing, the chloride diffusivity was reduced from 12.8 x 10$^{-12}$ m$^2$/s for the pure portland cement to 4.0, 3.1 and 3.2 x 10$^{-12}$ m$^2$/s for the 40, 60 and 80% slag contents, respectively. All these test results are in general agreement with other results reported in the literature [6,22]. Thus in Figure 11, there was hardly any effect on the chloride diffusivity for slag contents of less than about 25%, while for slag contents of 25 to 50%, there was a large drop in diffusivity, beyond which there was still a decrease but only to a smaller extent.

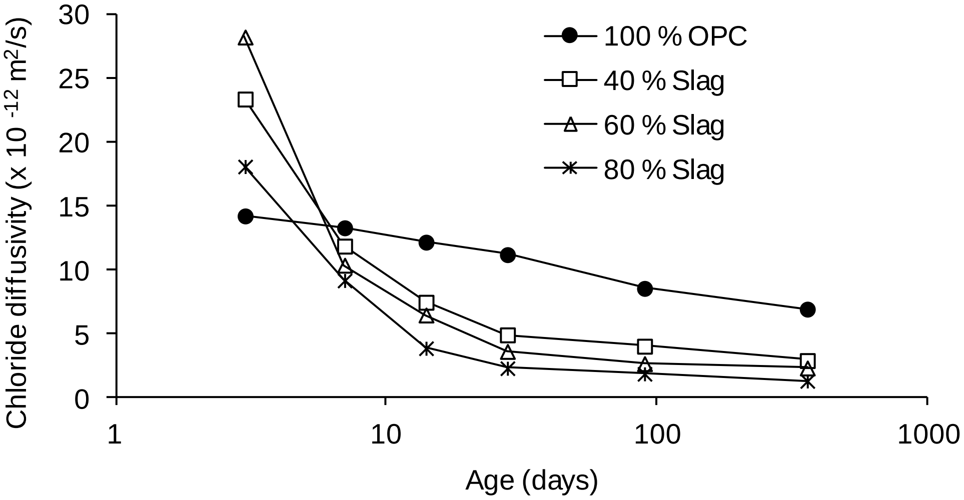

*Figure 9 – Effect of blast furnace slag on the chloride diffusivity of concrete (RCM) [23].*

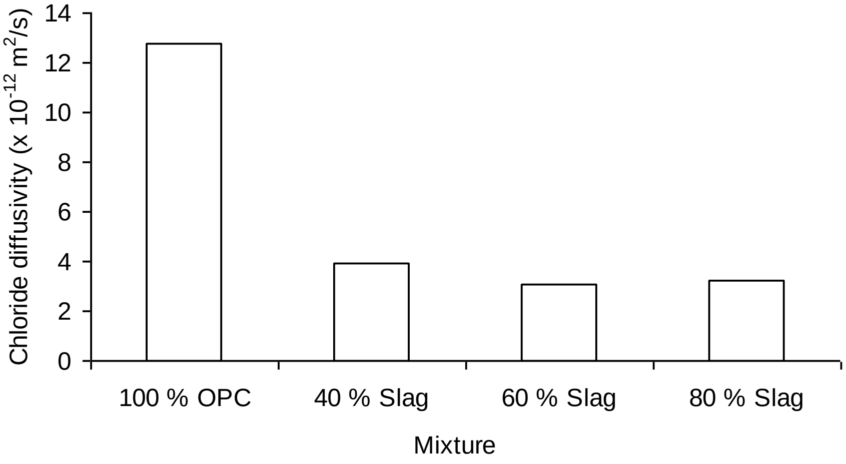

*Figure 10 – Effect of blast furnace slag on the chloride diffusivity of concrete (Immersion) [19].*

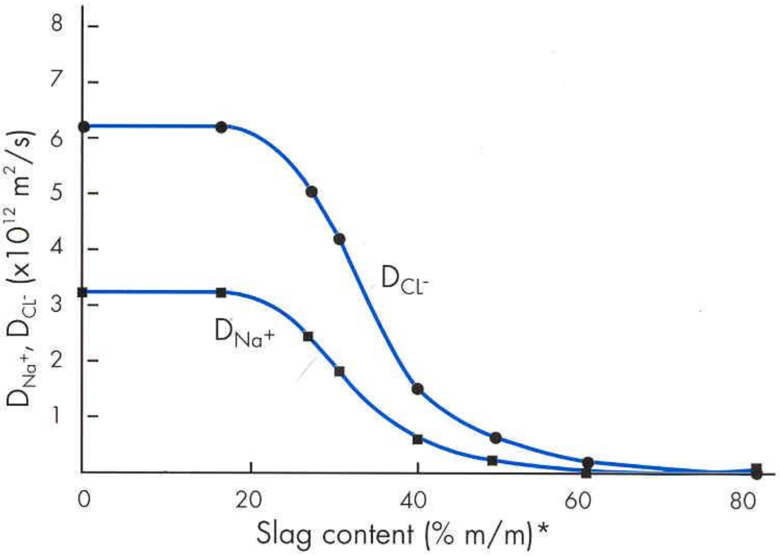

*Figure 11 – Effect of blast furnace slag on the diffusivity of pure cement paste at a water/binder ratio of 0.60 [24].*

For many of the replacement materials for portland cement, further beneficial effects on the resistance against chloride penetration can be reached by increased fineness of the replacement material. Thus, by using blast furnace slag with a Blaine fineness of up to about 16,000 cm$^2$/g, an extremely high resistance against chloride penetration was obtained [25]. Based on the Steady State Migration (SSM) method [26], the observed chloride diffusivity for the various types of this concrete varied in the range of 0.04 to 0.08 x 10$^{-12}$ m$^2$/s.

Although the chemical reactions of pozzolanic materials and blast furnace slags are quite different, the resulting effect on both microstructure and chemical composition of the pore solution in the concrete appears to be quite similar. In both cases, a substantially higher formation of CSH-gel with a higher amount of small gel pores (< 30 nm) and a smaller amount of large capillary pores compared to that of pure portland cements are formed. Thus, for the 80% slag cement shown in Figure 7, porosity measurements showed that as much as about 80% of the total porosity was made up by pores smaller than 200 Å, while for the portland cements, the corresponding number was only about 30% [18].

Investigations further indicate, that also the chloride binding capacity of the slag cements increases with increasing contents of slag, mainly due to the higher aluminate levels in the slag forming higher amounts of Friedel`s salt [27]. Also the substantially smaller amount of free lime in the hardened cement paste of slag changes the chemical composition of the pore solution in a beneficial way for the chloride diffusivity. However, a reduced amount of free lime in the hardened cement paste reduces the alkalinity of the pore solution, which may also reduce the critical level of chloride concentration for breaking the passivity of embedded steel. For a very dense concrete, however, such a reduced critical level of chloride concentration does not necessarily represent any practical durability problem. The slag also very much increases the electrical resistivity of the concrete in such a way that an ohmic control of the further corrosion process is obtained.

As already pointed out, even a pure diffusion of chloride ions into concrete from an external salt solution is a very complex transport process. As part of this process, also the chemical composition of the external salt solution is very important for the resulting penetration of chlorides [28]. This effect is clearly demonstrated in Figure 12, where a deeper chloride penetration from a salt solution based on $CaCl_2$ compared to that of NaCl is observed, while the chloride concentration in the external salt solutions was kept the same. Therefore, not only the permeability and the capacity of chloride binding but also the total ion exchange capacity of the system is very important for the resulting chloride penetration. Thus as demonstrated in Figure 12, the use of de-icing salts based on $CaCl_2$ give a more severe exposure for chloride penetration into concrete compared to that of NaCl in seawater.

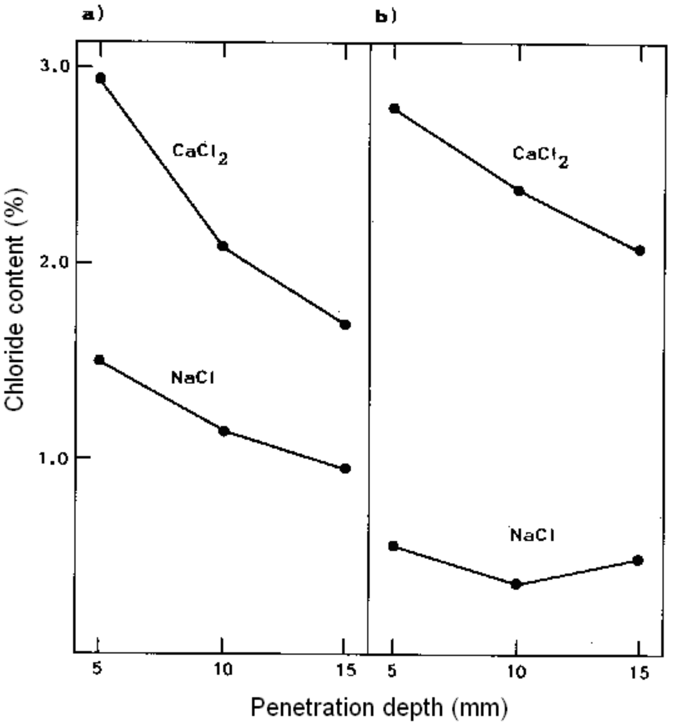

*Figure 12 – Chloride penetration (by weight of cement) into cement paste from two different types of salt solution of the same chloride concentration: a) after two days of hydration and b) after 40 days of hydration before exposure (Trætteberg, 1977, in Gjørv and Vennesland [29]).*

## 3. FREEZING AND THAWING

It is well known that the lower alkalinity of concrete based on granulated blast furnace slag cements generally increases the susceptibility to carbonation. As a result, the resistance to surface scaling from freezing and thawing may also be reduced compared to that of concrete based on other types of binder system. This reduced frost resistance appears to be somewhat different depending on the presence of salt or not in the environment. It is also well documented in the literature, however, that if only the concrete is dense enough, e.g. water/binder ratio of 0.40 or less, neither carbonation nor frost resistance of the concrete based on blast furnace slag cements appear to represent any durability problem. Thus, in The Netherlands where blast furnace slag cements have been widely used for a very long time, concretes with an upper water/binder ratio of 0.45 are generally considered to be frost resistant, even in salt containing environments [7]. Also, at the Treat Island Field Station at the east cost of Canada, concrete based on slag cements with up to 80% slag at a water/binder ratio of 0.40 still performed well after 25 years of very severe exposure to freezing and thawing in the tidal zone [13]. For most applications of concrete to marine environments, a water/binder ratio of 0.40 or less is typically being applied.

Before the concrete based on blast furnace slag cement with 70% slag was approved for application to the new city development project on Tjuvholmen in the harbour region of Oslo City [8], an extensive documentation program on the frost resistance of the given type of concrete was carried out [30]. Typically, this concrete had a cement content of 390 kg/m$^3$ (CEM III/B 42.5 LH HS) in combination with 39 kg/m$^3$ silica fume (10%) giving a water/binder ratio of 0.37. In order to improve the fresh concrete properties, the concrete was added a small amount of entrained air (3%). In addition to this basic type of concrete, the documentation program also included the testing of two other versions of the concrete mixture, one with a higher dosage of entrained air (6%), and as a reference, a concrete without any air entrainment. The documentation program was further based on two different types of test method with very different exposure conditions. One of the test series was based on the German CDF-method prEN12390-9 with 28 freeze-thaw cycles [31], while the other test series was based on the Swedish method SS 13 72 44 – 3 with 112 freeze-thaw cycles [32]. From both test series, it was concluded that all three versions of the concrete based on high volume slag cement showed a very good frost resistance regardless of the varying air void content. Based on this documentation, the given concrete with 3% entrained air was adopted for all the marine concrete structures with exposure to frost action.

## 4. CONCLUDING REMARKS

In Norwegian waters, chloride-induced corrosion of embedded steel has been the major threat and problem to the operation and safety of a large number of important concrete infrastructures for a very long time. For certain periods of the year, all these structures are being heavily exposed to the most severe combination of wave action and splashing of seawater. For much of the concrete construction work in Norwegian marine environments, the construction also takes place all year around. Therefore, the risk for early-age chloride exposure during concrete construction before the concrete has gained sufficient maturity and density is also very high. Thus, for several of the concrete structures along the Norwegian coastline, a deep chloride penetration took place already during concrete construction.

For important concrete infrastructures in marine environments it should always be very important to apply a concrete with a highest possible resistance against chloride penetration. For environmental conditions typical for Norwegian waters, a high early-age resistance against chloride penetration should also be very important. For such environmental conditions, the documentation as outlined and discussed in the present paper shows that concrete with a binder system based on granulated blast furnace slag would give a much better durability compared to that of other types of binder system.

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# Frost Resistance of Concrete Containing Secondary Cementitious Materials - Experience from Field and Laboratory Investigations

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## ABSTRACT

Concrete samples made from different binder types/combinations, including secondary cementitious materials, have been exposed at an exposure site in a highway environment for over 14 years. The resistance to internal and external frost damage has been regularly evaluated by measurements of change in volume and ultrasonic pulse transmission time. Here the results of 14 years' exposure are presented. The results are discussed with respect to previous studies of the effect of ageing in the laboratory and with respect to the test method for evaluating the scaling resistance of concrete, CEN/TS 12390-9. Suggestions of how to improve the test method with regard to ageing effects are presented.

**Key words**: Freeze/thaw, scaling, ageing, carbonation, field test, laboratory test, secondary cementitious materials

## 1. INTRODUCTION

Resistance to external and internal frost damage is of great importance in determining the durability of concrete in the Scandinavian countries, as well as in other European countries with cold climates. Test methods such as CEN-TS 12390-9 [1] and (for internal damage) CEN

TR 15177 [2] have been developed to determine whether concrete qualities are resistant to external damage (scaling).

However, these test methods have been developed primarily on the basis of experience with traditional concrete made with ordinary Portland cement (CEM I). When new types of concrete are introduced – for example, with secondary cementitious materials, filler materials, new admixtures, etc. – we do not know how to evaluate the test results, or even whether the freeze/thaw test methods used are relevant. More knowledge and experience of the frost resistance of these new concrete qualities in the field as well as in laboratory tests are needed.

One way to acquire this experience is to expose concrete specimens to representative outdoor environments. Such an investigation was started in Sweden in the mid-nineties. Three field exposure sites were established in the south-west of the country: one in a highway environment beside highway 40 (60 km east of Gothenburg), one in a marine environment at Träslövsläge harbour (80 km south of Gothenburg), and one in an environment without salt exposure on SP's premises in Borås (70 km east of Gothenburg).

A large number of concrete mixtures of varying quality with different binder types/combinations, different water/binder ratios and different air contents have been exposed for more than fourteen years at these test sites. The external and internal frost damage has been regularly evaluated by measurements of the volume change of the specimens and the change in ultrasonic transmission time through each specimen. The results after ten years' exposure at the three field test sites are presented in [4]. The results after ten years' exposure clearly indicated the highway environment as being the most aggressive with regard to external frost damage. The influence of climate on the internal frost damage was less pronounced. In this paper, results after fourteen years' exposure at the highway exposure site are presented. Results from concrete qualities with the following binder types/combinations are included: CEM I, CEM II/A-LL, CEM II/A-S, CEM I + 30% slag, CEM I + 5% silica, CEM III/B, CEM II/A-V and CEM II/A-V + 3.8% as binder.

Investigations carried out to study the effect of ageing on the salt-frost resistance of concrete show that ageing has a strong influence on the salt-frost resistance of concrete, and that carbonation is the most dominant ageing effect [3]. The effect of carbonation is, however, different for different binder types. For example, carbonation leads to an improved salt-frost resistance for concrete with CEM I as binder, while the effect of carbonation is the opposite for concrete with CEM III/B as binder, leading to a poorer salt-frost resistance.

CEN-TS 12390-9 [1] is currently in use, and it specifies that specimens are to be cured in normal air for a relatively short time. This means that the effect of carbonation may not be fully taken into account. CEN-TS 12390-9 [1] will be revised in the next couple of years, as part of the work within CEN/TC51/WG12/TG4. It is important to make changes in this revision that lead to the effect of carbonation being better taken into account.

## 2. MATERIALS AND SPECIMENS

The binder types/combinations studied in this investigation are shown in Table 1. For the chemical compositions, see [5].

*Table 1 – Binder types/combinations investigated*

| Binder type/combination | | Comments |
|---|---|---|
| 1 | CEM I$^{1)}$ | Low alkali, sulphur-resistant |
| 2 | CEM I$^{1)}$ + 5 % silica by binder weight | Silica in the form of slurry |
| 3 | CEM II/A-LL | Cement with 15% limestone filler |
| 4 | CEM II/A-S | Finnish cement with ~15% slag |
| 5 | CEM I$^{1)}$ + 30 % slag by binder weight | Ground blast furnace slag added in the mixer |
| 6 | CEM III/B | Dutch slag cement, ~70% slag |
| 7 | CEM II/A-V | Norwegian cement with up to 20% flyash |
| 8 | CEM II/A-V + 3,8 % silica by binder weight | Silica in the form of slurry |

$^{1)}$ CEM I = Degerhamn Standard is a low-alkali, sulphur-resistant cement

For binder type/combinations 1 to 6, ten different concrete qualities were produced for each binder type/combination. Concrete qualities with five different water/binder (w/b) ratios (0.30, 0.35, 0.40, 0.50, 0.75), and with and without entrained air, were produced for all binder combinations. 0–8 mm natural and 8–16 mm crushed aggregate were used for all mixes. A naphthalene-based plasticizer, Melcrete, was used for mixtures with w/b-ratios of 0.40 or lower. The air-entraining agent used, L16, is a tall oil derivative. A summary of the concrete constituents and properties is presented in Table 2: for a complete presentation, see [5].

Three concrete qualities were produced of binder type/combination 7 (one with w/b-ratios 0.40 and two with 0.45), all with entrained air. A single concrete quality was produced of binder type/combination 8 (w/b-ratio 0.40), with entrained air. Concrete qualities with binder type/combinations 7 and 8 were produced by the cement producer NORCEM in Norway. For details about the concrete compositions, see Table 2 and [6].

*Table 2 – Concrete constituents and properties*

| Binder type | w/b-ratio | Equiv. w/c-ratio$^{(1}$ | Cement ($kg/m^3$) | SCM$^{(2}$ ($kg/m^3$) | aea$^{(3}$ | Air content fresh (%) | Slump (mm) | Compressive strength (MPa) | | Scaling ($kg/m^2$)$^{(6}$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | SS$^{(4}$ | Recalc$^{(5}$ | 28 | 56 |
| CEM I | 0.30 | 0.30 | 500 | - | Yes | 4.8 | 240 | 95 | 87 | 0.02 | 0.04 |
| | 0.35 | 0.35 | 450 | - | Yes | 4.8 | 190 | 95 | 87 | 0.05 | 0.09 |
| | 0.40 | 0.40 | 420 | - | Yes | 4.6 | 125 | 67 | 60 | 0.01 | 0.02 |
| | 0.50 | 0.50 | 370 | - | Yes | 4.6 | 90 | 49 | 44 | 0.02 | 0.02 |
| | 0.75 | 0.75 | 260 | - | Yes | 4.7 | 100 | 21 | 18 | 0.13 | 0.14 |
| | 0.30 | 0.30 | 500 | - | No | 1.1 | 120 | 102 | 93 | 0.16 | 0.26 |
| | 0.35 | 0.35 | 450 | - | No | 1.2 | 140 | 91 | 83 | 1.94 | 4.39 |
| | 0.40 | 0.40 | 420 | - | No | 0.8 | 130 | 87 | 79 | 3.11 | 7.92 |
| | 0.50 | 0.50 | 385 | - | No | 0.8 | 70 | 56 | 50 | 5.09 | 14.5 |
| | 0.75 | 0.75 | 265 | - | No | 0.9 | 60 | 31 | 27 | 4.34 | >15 |
| 95% CEM I + 5% silica | 0.30 | 0.29 | 475 | 25 | Yes | 4.6 | 100 | 103 | 94 | 0.04 | 0.12 |
| | 0.35 | 0.33 | 427.5 | 22.5 | Yes | 4.5 | 90 | 91 | 83 | 0.02 | 0.04 |
| | 0.40 | 0.38 | 399 | 21 | Yes | 4.8 | 105 | 72 | 65 | 0.02 | 0.04 |
| | 0.50 | 0.48 | 361 | 19 | Yes | 4.6 | 70 | 57 | 51 | 0.02 | 0.03 |
| | 0.75 | 0.71 | 237.5 | 12.5 | Yes | 4.3 | 70 | 25 | 22 | 0.19 | 0.20 |
| | 0.30 | 0.29 | 475 | 25 | No | 1.1 | 125 | 121 | 111 | 0.12 | 0.20 |
| | 0.35 | 0.33 | 427.5 | 22.5 | No | 1.1 | 90 | 105 | 96 | 0.36 | 0.89 |
| | 0.40 | 0.38 | 399 | 21 | No | 0.5 | 100 | 84 | 76 | 1.67 | 3.25 |
| | 0.50 | 0.48 | 370.5 | 19.5 | No | 1.2 | 60 | 67 | 60 | 1.86 | 4.61 |
| | 0.75 | 0.71 | 256.5 | 13.5 | No | 0.3 | 75 | 35 | 31 | 3.45 | 6.58 |

| Binder type | w/b-ratio | Equiv. w/c-ratio(1 | Cement (kg/m$^3$) | SCM(2 (kg/m$^3$) | aea(3 | Air content fresh (%) | Slump (mm) | Compressive strength (MPa) | | Scaling (kg/m$^2$)(6 | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | SS(4 | Recalc(5 | 28 | 56 |
| CEM II/A-S | 0.30 | - | 520 | - | Yes | 4,4 | 70 | 62 | 56 | 0.09 | 0.11 |
| | 0.35 | - | 450 | - | Yes | 4,5 | 100 | 62 | 56 | 1.40 | 2.23 |
| | 0.40 | - | 420 | - | Yes | 4,5 | 80 | 53 | 47 | 1.75 | 2.45 |
| | 0.50 | - | 380 | - | Yes | 4,8 | 100 | 39 | 34 | 0.15 | 0.16 |
| | 0.75 | - | 260 | - | Yes | 4,7 | 100 | 25 | 22 | 1.12 | 1.25 |
| | 0.30 | - | 540 | - | No | 2,2 | 30 | 69 | 62 | 0.32 | 0.42 |
| | 0.35 | - | 450 | - | No | 2,6 | 35 | 64 | 57 | 2.37 | 4.06 |
| | 0.40 | - | 420 | - | No | 2,0 | 90 | 58 | 52 | 3.93 | 6.71 |
| | 0.50 | - | 400 | - | No | 1,7 | 65 | 48 | 43 | 5.28 | 7.65 |
| | 0.75 | - | 275 | - | No | 0,5 | 100 | 30 | 26 | TD | TD |
| CEM II/A-LL | 0.30 | 0.30 | 520 | - | Yes | 4,4 | 110 | 89 | 81 | 0.03 | 0.05 |
| | 0.35 | 0.35 | 450 | - | Yes | 4,3 | 110 | 85 | 77 | 0.14 | 0.25 |
| | 0.40 | 0.40 | 420 | - | Yes | 4,6 | 90 | 72 | 65 | 0.11 | 0.12 |
| | 0.50 | 0.50 | 390 | - | Yes | 4,8 | 70 | 52 | 46 | 0.17 | 0.20 |
| | 0.75 | 0.75 | 260 | - | Yes | 4,7 | 70 | 34 | 30 | 2.92 | 5.26 |
| | 0.30 | 0.30 | 530 | - | No | 2,3 | 100 | 95 | 87 | 0.16 | 0.28 |
| | 0.35 | 0.35 | 470 | - | No | 2,4 | 115 | 86 | 78 | 0.52 | 1.05 |
| | 0.40 | 0.40 | 420 | - | No | 2,4 | 110 | 76 | 69 | 3.04 | 5.67 |
| | 0.50 | 0.50 | 400 | - | No | 1,8 | 70 | 64 | 57 | 5.05 | 11.6 |
| | 0.75 | 0.75 | 280 | - | No | 1,2 | 75 | 36 | 32 | TD | TD |
| 70% CEM I + 30% slag | 0.30 | 0.34 | 350 | 150 | Yes | 4.8 | 230 | 90 | 82 | 0.03 | 0.05 |
| | 0.35 | 0.40 | 315 | 135 | Yes | 4.8 | 130 | 86 | 78 | 0.09 | 0.14 |
| | 0.40 | 0.45 | 294 | 126 | Yes | 4.4 | 110 | 65 | 58 | 0.04 | 0.07 |
| | 0.50 | 0.57 | 259 | 111 | Yes | 4.8 | 80 | 49 | 44 | 0.02 | 0.03 |
| | 0.75 | 0.85 | 175 | 75 | Yes | 4.4 | 100 | 20 | 17 | 0.49 | 0.54 |
| | 0.30 | 0.34 | 350 | 150 | No | 0.7 | 220 | 101 | 92 | 0.10 | 0.13 |
| | 0.35 | 0.40 | 315 | 135 | No | 1.1 | 140 | 91 | 83 | 1.78 | 3.61 |
| | 0.40 | 0.45 | 294 | 126 | No | 0.9 | 120 | 78 | 71 | 1.78 | 3.83 |
| | 0.50 | 0.57 | 273 | 117 | No | 1.3 | 80 | 52 | 46 | 0.86 | 1.94 |
| | 0.75 | 0.85 | 185.5 | 79.5 | No | 0.5 | 80 | 25 | 22 | 1.58 | 4.37 |
| CEM III (~70% slag) | 0.30 | 0.30 | 520 | - | Yes | 4.8 | 200 | 78 | 71 | 0.25 | 0.36 |
| | 0.35 | 0.35 | 460 | - | Yes | 4.7 | 200 | 74 | 67 | 0.43 | 0.62 |
| | 0.40 | 0.40 | 420 | - | Yes | 4.3 | 120 | 61 | 55 | 0.57 | 0.85 |
| | 0.50 | 0.50 | 380 | - | Yes | 4.5 | 70 | 46 | 41 | 0.99 | 1.66 |
| | 0.75 | 0.75 | 255 | - | Yes | 4.4 | 90 | 26 | 23 | 2.05 | 3.16 |
| | 0.30 | 0.30 | 520 | - | No | 0.8 | 200 | 99 | 90 | 0.22 | 0.28 |
| | 0.35 | 0.35 | 470 | - | No | 0.7 | 200 | 80 | 72 | 0.49 | 0.65 |
| | 0.40 | 0.40 | 420 | - | No | 0.9 | 125 | 68 | 61 | 0.84 | 1.14 |
| | 0.50 | 0.50 | 400 | - | No | 1.0 | 65 | 54 | 48 | 1.21 | 1.61 |
| | 0.75 | 0.75 | 265 | - | No | 0.1 | 100 | 31 | 27 | 3.94 | 6.89 |
| CEM II/A-V | 0.40 | 0,40 | 460 | - | Yes | 5.6 | 175 | 56 | 50 | 0.09 | 0.20 |
| | 0.45 | 0.45 | 400 | - | Yes | 4.5 | 125 | 49 | 44 | 0.15 | 0.17 |
| | 0.45 | 0.45 | 420 | - | Yes | 4.3 | 70 | 51 | 45 | 0.26 | 0.34 |
| CEM II/A-V + 3,8% silica | 0.40 | 0.39 | 400 | 16 | Yes | 4.4 | 150 | 61 | 55 | 0.23 | 0.31 |

(1 Equiv. w/c-ratio=water/(cement + 2∗silica + 0.6∗slag). Not applicable for CEM II/A-S, CEM II/A-LL, CEM III and CEM II/A-V.

(2 SCM – Secondary Cementitious Materials

(3 AEA – Air Entraining Agent

(4 Dry stored cubes tested in accordance with SS 13 72 10 [7] at the age of 28 days

(5 Recalculated to wet stored cubes in accordance with $f_{wet,cube} = 0.76*(f_{dry,cube})^{1.04}$

(6 In accordance with the 'Slab test', SS 13 72 44 [8], freeze/thaw started at the age of 31 days

TD = Totally disintegrated

All concrete batches with binder type/combinations 1 to 6 were produced in the autumn of 1996, and a number of 150 mm cubes were cast from each batch. The cubes were demoulded 24 hours after casting, and stored in lime-saturated water for six days. They were then stored in a climate chamber (50% RH at 20 °C) for a period of between one and a half and three months. Between eight and twelve days before the specimens were placed at the field test sites, the cubes were cut, resulting in two specimens with the shape of a half 150 mm cube with one cut surface and the rest mould surfaces. After cutting, the specimens were stored in a climate chamber (50% RH at 20 °C) until placed at the test sites. During this second conditioning period, the volume of, and transmission time through, each specimen were measured. Two specimens of each mixture were then placed at each test site.

Concrete batches with binder type/combinations 7 and 8 were produced in 1997 by the cement producer NORCEM in Norway. After demoulding and storage in lime-saturated water for six days, the specimens were sent to SP in Borås, Sweden, where the specimens were treated as described above. For concrete qualities produced with these binder types/combinations, two to four specimens from each quality were placed at each test site.

At the highway environment test site, the specimens were placed in steel frames close to the road, so that they were splashed by the passing traffic. The specimens were exposed with the cut surface facing upwards.

## 3. TEST PROCEDURES

In order to be able to detect both internal and external frost damage, the change in volume and ultrasonic pulse transmission time were measured regularly. The first measurement was carried out before placing the specimens at the test sites. The specimens at the highway site have subsequently been measured once a year during the first years of exposure, and thereafter every second to every fourth year.

The volumes of the specimens are calculated from results obtained from measuring the weight of the specimens first in water and then in air. The ultrasonic pulse transmission time through the specimen (150 mm) is calculated as the mean of three measurement positions, where possible, on each specimen.

The following laboratory tests were carried out on each concrete mix in order to determine the concrete characteristics (results are given partly in Table 2 above and fully in [5] for binder type/combinations 1 to 6, and in [6] for binder type/combinations 7 and 8):

Testing the fresh concrete:

- Air content
- Density
- Slump
- Remoulding test

Testing the hardened concrete:

- Compressive strength in accordance with SS 13 72 10 [7]
- Salt/frost resistance in accordance with SS 13 72 44 [8]
- Microscopical determination of the air void system, in principal in accordance with ASTM C 457 [9].

## 4. RESULTS

Figures 1 and 2 present results from measurements of the volume change (%) after fourteen years of exposure at the highway test site. The reference value is the initial volume before exposure. Figure 1 shows the results for concrete produced without entrained air, while Figure 2 shows the results for concrete with entrained air (4–5%). Each point is the mean value of measurements on two specimens for concrete qualities produced with binder types/combinations 1 to 6. For concrete qualities with binder type/combinations 7 and 8, each point is the mean value of two to four specimens.

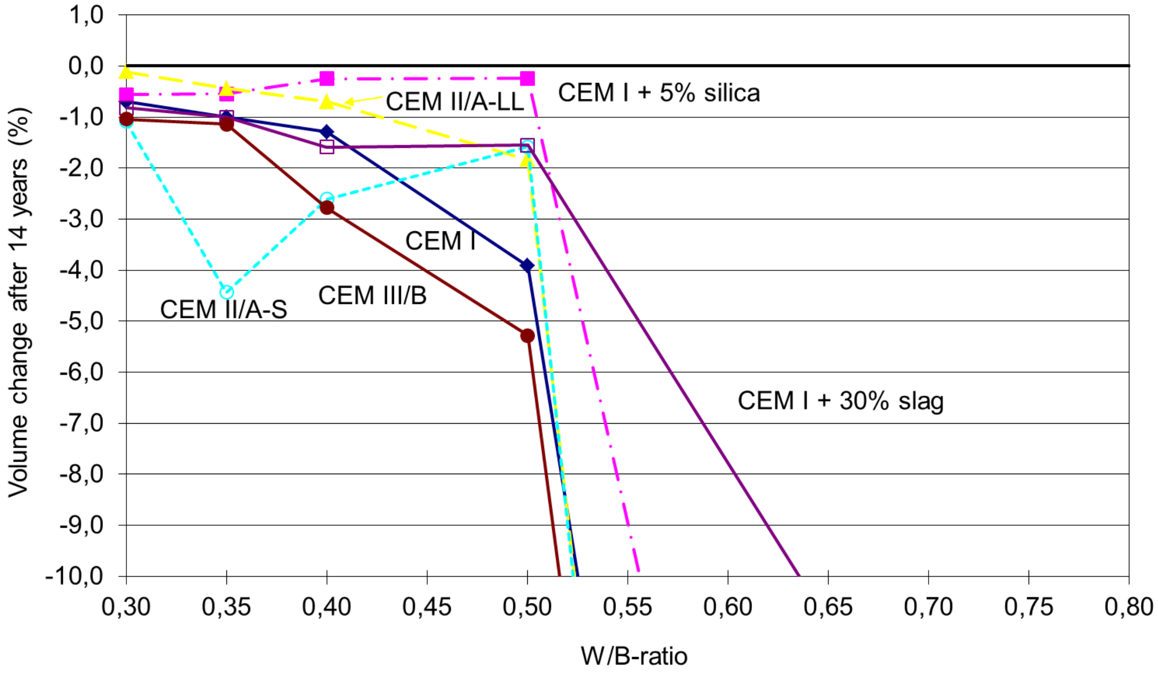

*Figure 1 - Volume change after fourteen years at the highway exposure site. Concrete with different binder combinations and water/binder ratios. No entrained air.*

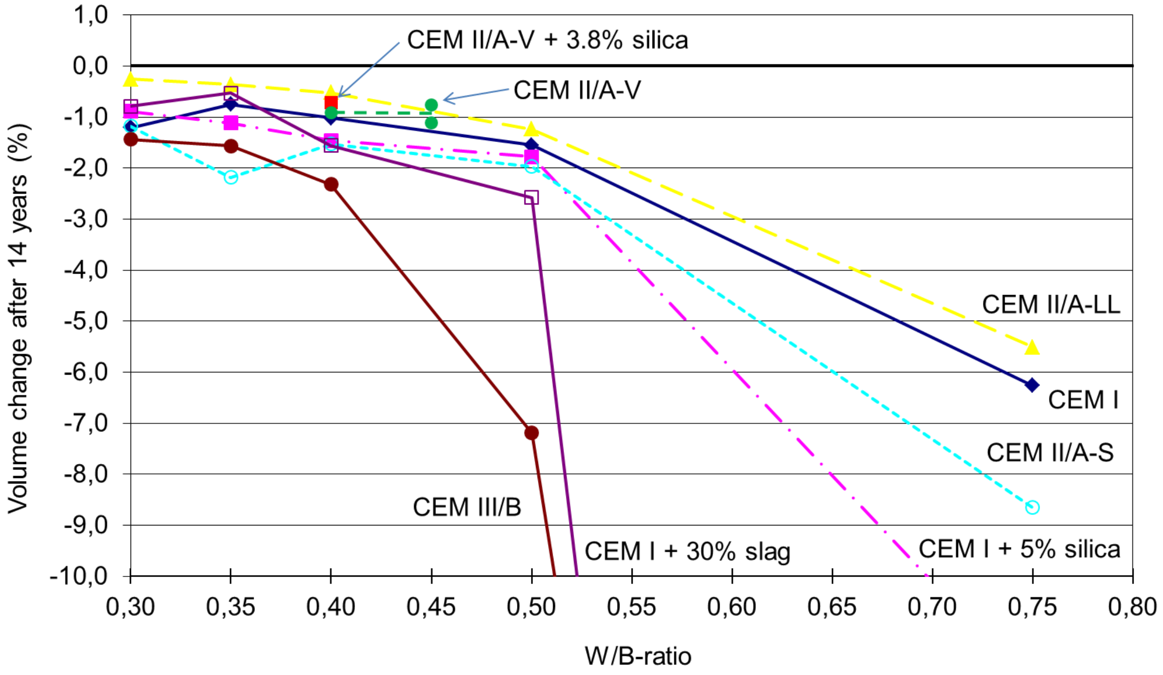

*Figure 2 – Volume change after fourteen years at the highway exposure site. Concrete with different binder combinations and water/binder ratios. With entrained air (4–5%).*

Table 3 shows the change in transmission time (%) after fourteen years' exposure at the highway test site. The reference value is that of measurements before exposure. Each point is the mean value of up to three measurements on each test specimen. No value is presented for some qualities with a w/b-ratio of 0.75: this is because damage to the concrete surfaces was so severe that measurements were not possible.

*Table 3 – Change in transmission time (%) after fourteen years at the highway exposure site. Concrete with different binder types/combinations, water/binder ratios and with and without entrained air.*

| Concrete mix \ w/b-ratio | 0.30 | 0.35 | 0.40 | 0.45 | 0.50 | 0.75 |
|---|---|---|---|---|---|---|
| CEM I, air | -3 | -2 | -2 | - | -2 | -8 1) |
| CEM I, no air | -4 | -3 | -2 | - | -3 | +10 1) |
| CEM I + 5% silica, air | -2 | -2 | 0 | - | -2 | -10 1) |
| CEM I + 5% silica, no air | -2 | -2 | + 3 | - | +13 | +31 1) |
| CEM II/A-LL, air | -6 | -6 | -5 | - | -4 | -2 |
| CEM II/A-LL, no air | -6 | -5 | -3 | - | -2 | +3 1) |
| CEM II/A-S, air | -5 | -3 | +2 | - | +6 | +5 |
| CEM II/A-S, no air | +1 | +6 | -1 | - | -0 | +3 1) |
| CEM I + 30% slag, air | -3 | -3 | -2 | - | +1 | -18 1) |
| CEM I + 30% slag, no air | -5 | -3 | -3 | - | -6 | -14 1) |
| CEM III/B, air | -4 | -3 | -1 | - | -1 1) | TD |
| CEM III/B, no air | -2 | -3 | -2 1) | - | -3 1) | TD |
| CEM II/A-V, air | - | - | +3 | 0; -3 | - | - |
| CEM II/A-V + 3,8% silica, air | - | - | -3 | - | - | - |

1) Result after 10 years. No detection could be made after 14 years because of to severe surface damage.

TD = Totally disintegrated

## 5. DISCUSSION

### 5.1 External frost damage

For concrete qualities with entrained air and with a w/b-ratio of 0.75, all qualities are more or less damaged after fourteen years' exposure at the highway test site, Figure 2. The most severely damaged are concretes CEM III/B and CEM I + 30% slag as binder, less damaged are CEM I and CEM II/A-LL. All concrete qualities with a w/b-ratio of 0.50 or lower and with entrained air, except those with CEM III as binder, show relatively small volume changes. CEM III with a w/b-ratio of 0.50, however, shows significant damage.

For concrete without entrained air exposed at the highway exposure site, all concrete qualities with a w/b-ratio of 0.75 show severe scaling, Figure 1. For concrete with a w/b-ratio of 0.5, the quality with CEM III/B as binder shows the highest scaling. For concrete with w/b-ratios 0.4 and below, the differences in scaling are relatively small. However, concrete quality CEM II/A-S with a w/b-ratio of 0.35 shows a much higher scaling than do other concrete qualities. The major part of this scaling occurred during the first winter, after which the scaling was very small. One explanation is that there is a problem with the compatibility between the cement and the plasticizer used, resulting in a poor air void structure. The plasticizer was used for qualities with w/b-ratios 0.40 and lower. From Figure 1 it can be seen that, for the qualities with w/b-ratios 0.40 and 0.35, the scaling is significantly higher than for the quality with a w/b-ratio of 0.50. The same tendency can be seen for concrete with entrained air and with a w/b-ratio of 0.35 in Figure 2. In addition, the results from testing in the laboratory indicate lower scaling resistance for concrete with w/b-ratios 0.35 and 0.40 compared to 0.50 (see Table 2), indicating a possible compatibility problem between the cement and plasticizer.

Results after five years' exposure, presented in [3], and after ten years' exposure, presented in [4], show an increase in volume for some qualities without entrained air with CEM I + 5% silica as binder and with a w/b-ratio over 0.35. An increase in volume is probably caused by internal damage, i.e. micro-cracks. A limitation of the volume measurement procedure is that the measured volume is the net volume of both a negative and a positive element: in the forms considered here this may be the result of a volume decrease due to surface scaling and a volume increase due to internal cracking. Concrete qualities with an apparent volume loss might, therefore, also have a small increase in volume caused by internal cracking without this being observed. It is, therefore, important to complement volume measurements with other techniques, such as ultrasonic pulse transmission time measurement, in order to detect internal damage.

In general, the volume changes for concrete with high water/binder ratios and entrained air are less than for concrete without entrained air (compare Figure 1 with Figure 2). However, this is not valid for concrete qualities with CEM III/B as the binder. The volume change for qualities with CEM III/B as the binder and with entrained air is of the same order of magnitude as that for concrete without entrained air (w/b-ratios 0.50 and 0.75). For these qualities, entrained air does not improve the scaling resistance. This behaviour is confirmed by freeze/thaw testing in the laboratory, Table 2. For concrete with CEM III/B as the binder, the air-entrained qualities show damage of the same order of magnitude as for concrete without air. For concrete with other binder types in this investigation, a significant improvement in scaling resistance is seen, as expected, for qualities with entrained air compared to qualities without entrained air.

## 5.2 Internal frost damage

Table 3 shows the percentage change in transmission time after fourteen years' exposure at the highway exposure site. A negative value (decrease in transmission time through the specimen with age) is expected for sound, undamaged materials due to the densification of the paste as a result of continued hydration. A positive value indicates possible internal damage. The results presented in Table 3 show that a number of concrete qualities probably have internal damage. Most concrete qualities without entrained air and with a w/b-ratio of 0.75 show indications of internal damage. For concrete with CEM III/B as part of the binder, the surfaces of the specimens exposed at the highway exposure site were too severely damaged to be able to measure ultrasonic transmission time.

Comparing the results after fourteen years in Table 3 with the results after ten years presented in [4] shows that in general only small changes have taken place. However, for concrete qualities with CEM II/A-S, both with and without air, the results after fourteen years indicate possible internal damage. This has not been verified by, for example, microscopical examination, and needs to be examined during the next round of measurements.

Combining the results from volume measurements with the transmission time measurements gives clear indications of internal damage for the concrete qualities with CEM I + 5% silica as binder and without entrained air, also for concrete with w/b-ratios down to 0.40. Both an increase in volume and an increase in transmission time clearly indicate internal damage, probably micro-cracking. The surfaces of the qualities that show increased transmission time without an increase in volume are too severely damaged to permit the detection of an increase in volume due to internal cracking. Microscopic techniques, such as the analysis of polished sections or thin sections, has been used to look for further evidence of internal damage, and the results were confirmed for some qualities after five years' exposure at the exposure sites [10].

From the results described above, it can be noted that concrete with CEM I, CEM I + 5% silica, or CEM II/A-LL as part of the binder with entrained air and a water/binder ratio of 0.50 or lower, resists damage from frost and salt/frost in an aggressive highway environment, for at least fourteen years of exposure. The same can be noted for concrete with CEM II/A-V and CEM II/A-V + 3.8% as binder with entrained air and a water/binder ratio of 0.45 or lower. For concrete with CEM I + 30% slag as part of the binder with entrained air, this is valid for concrete with a water/binder ratio of 0.40 or lower. For this binder combination, concrete with a w/b-ratio 0.50 and with entrained air shows a somewhat greater volume loss than concrete produced with other binder types/combinations. For concrete with CEM II A/S as part of the binder and a w/b-ratio of 0.50 or lower with entrained air, the loss of volume is comparable with that of the other binder types. However, after fourteen years of exposure there are indications of possible internal damage that need to be further examined.

Our results show that concrete containing large amounts of slag as binder are less resistant to external salt/frost damage than concrete with the other binder types. After fourteen years of exposure at the highway exposure site, concrete with CEM III suffers from severe scaling, even with a w/b-ratio below 0.5 and with entrained air. The results regarding concrete with high slag content are in agreement with those from an extensive field exposure investigation presented in [11, 12, 13]. In that investigation, a large number of concrete qualities with different amounts of slag in the binder were exposed to the marine climate at the Treat Island exposure site, Canada. Results from that investigation clearly show that salt/frost resistance decreases with increasing amounts of slag as part of the binder; a result that is confirmed by the present investigation. As in the present investigation, the investigation at Treat Island showed the positive effect of a low water/binder ratio on the salt/frost resistance of concrete. The negative effects of high slag contents in the binder on the salt/frost resistance of concrete have been reported by several researchers [14, 15, 16, 17]. One probable explanation for this negative effect is the coarsening of the pore structure found in the carbonated skin of concrete containing slag [3, 14, 16, 18]. Another probable explanation, presented in [16], is the existence of metastable carbonates in the carbonated zone of concrete rich in slag.

## 5.3 Correlation between laboratory and field tests

When testing durability, such as salt/frost resistance, in the laboratory, results are wanted that are relevant to durability in field conditions. In the present investigation, each concrete quality was tested in the laboratory at the prescribed age of 28 days in accordance with the Swedish Standard for salt/frost resistance, SS 13 72 44 (the 'Slab test') [8]. The slab test is in principal in agreement with the reference test procedure described in CEN/TS 12390-9.

Figure 3 shows results from the laboratory tests and the volume change after fourteen years of highway exposure. The diagram shows the scaling (kg/m²) after 56 freeze/thaw cycles as a function of the volume loss (%) after fourteen years' highway exposure. The acceptance criterion in the laboratory test is 1 kg/m$^2$ (illustrated by a horizontal line). An acceptance criterion of 2–3% by volume (shown by the vertical zone) after fourteen years' exposure has been chosen for the field exposure specimens, corresponding to scaling of approximately 1 kg/m$^2$. Filled symbols represent concrete with entrained air. Symbols with a white centre represent concrete without entrained air.

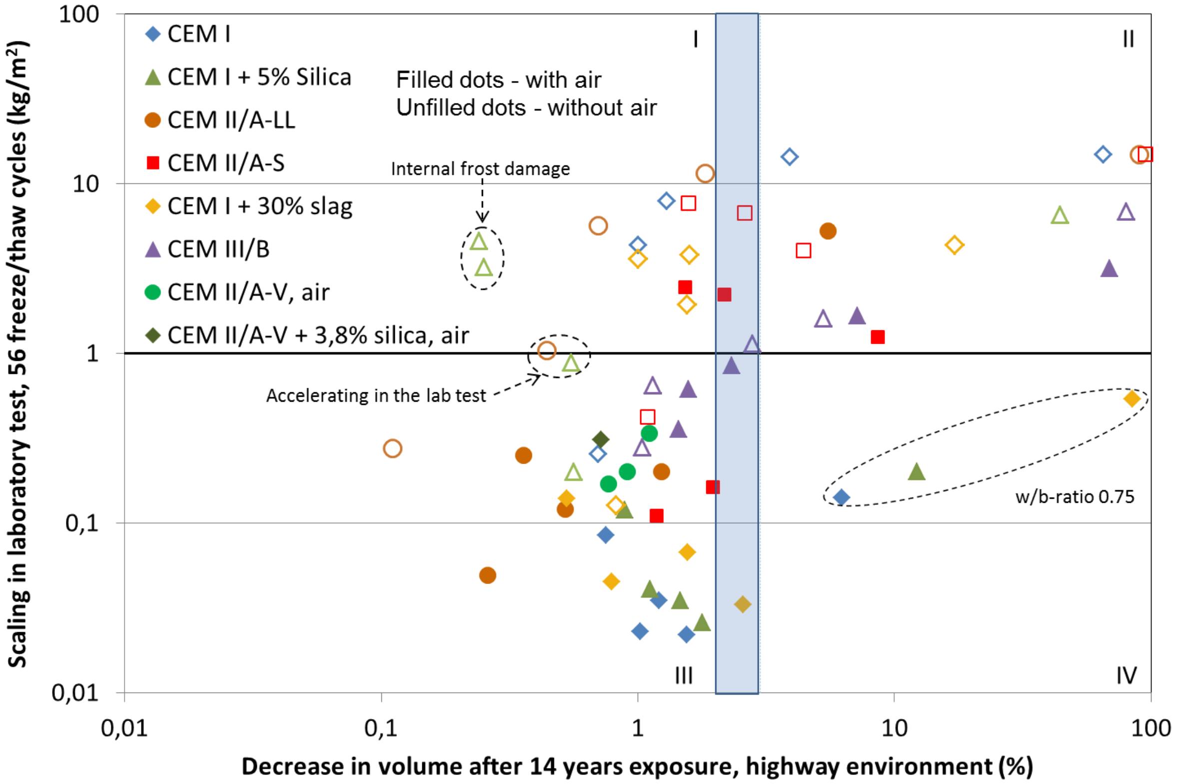

*Figure 3 – Scaling resistance (tested in the laboratory by the slab test) as a function of the decrease in volume for specimens exposed in the highway environment for fourteen winter seasons. Filled symbols represent concrete with entrained air. Symbols with a white centre represent concrete without entrained air.*

The results presented in Figure 3 show that only three qualities fall into Quadrant IV, which is the worst case, where they are accepted by the test method but fail in field exposure. These are air-entrained qualities, however, with high water/binder ratios (0.75). The standard test method is primarily intended to be used for bridge concrete, with entrained air and with a w/b-ratio below 0.5. Two qualities, both with entrained air and a w/b-ratio of 0.50 or below, are in the acceptance zone between Quadrants III and IV. Both of these qualities contain slag as part of the binder (CEM III and CEM I + 30% slag). This is an indication that the laboratory test method may overestimate the scaling resistance of concrete containing a medium to high content of slag as part of the binder. The damage development for these qualities needs to be investigated thoroughly in the future.

Most qualities fall into Quadrants II or III, which means that the test method and 'reality' correspond. Some concrete qualities fall into Quadrant I, which means that the test method rejects them. However, as the concrete in Quadrant I shows only limited damage in the field, the test method results are on the side of safety. Only two of these qualities have entrained air, both with binder type CEM II/A-S. All other qualities in Quadrant I are without entrained air, which makes them particularly susceptible to frost damage. During the first fourteen years, the climate has not been aggressive enough to damage these qualities significantly. However, one winter season with a more aggressive climate might cause internal damage as well as scaling on these qualities without entrained air, moving them into Quadrant II. Two concrete qualities show an increase in volume (after five and ten years' exposure) and an increased transmission time, indicating internal frost damage. These qualities also fail the acceptance criterion when tested in the laboratory.

On the whole, the results for concrete with w/b-ratios equal to or below 0.5, and with entrained air, indicate that the slab test classifies most concrete qualities as could be expected, Figure 3. However, the results after fourteen years show indications that concrete containing medium to high contents of slag as part of the binder, with entrained air and a w/b-ratio of as low as 0.40, show higher scaling in the field than that expected from results from the laboratory test. This is discussed further below.

### 5.4 Effect of ageing on the scaling resistance of concrete

Two main questions regarding the results from this investigation after fourteen years of exposure at the highway exposure site need to be further discussed. The first relates to the concrete qualities with low scaling resistance in the laboratory test but with only limited scaling after fourteen years of exposure, i.e. the qualities in Quadrant I in Figure 3. The second question relates to the effect of slag as part of the binder on the scaling resistance, and the indications that results from laboratory tests for concrete with medium to high content of slag as part of the binder may not be on the safe side, i.e. the concrete qualities that fall into the acceptance zone between Quadrants III and IV in Figure 3.

One possible explanation for the limited scaling in the field for the concrete qualities in Quadrant I is a positive effect of ageing. In a field investigation reported in [19], it was found that concrete aged and exposed in a marine climate showed better scaling resistance when tested in the laboratory after ageing than did virgin concrete, Figure 4. The results presented in Figure 4 show that concrete aged for three years at a marine exposure site has a higher scaling resistance than when tested at an age of 28 days. In this investigation concrete with CEM I and CEM I + up to 10% silica, with a w/b-ratio between 0.35 and 0.75, with and without entrained air was studied. The positive effect of ageing is especially evident for concrete without entrained air, which is in analogy with the results seen in Quadrant I in Figure 3. These results indicate that ageing of the concrete surface leads to a higher scaling resistance, at least for concrete with CEM I or CEM I with some silica as part of the binder.

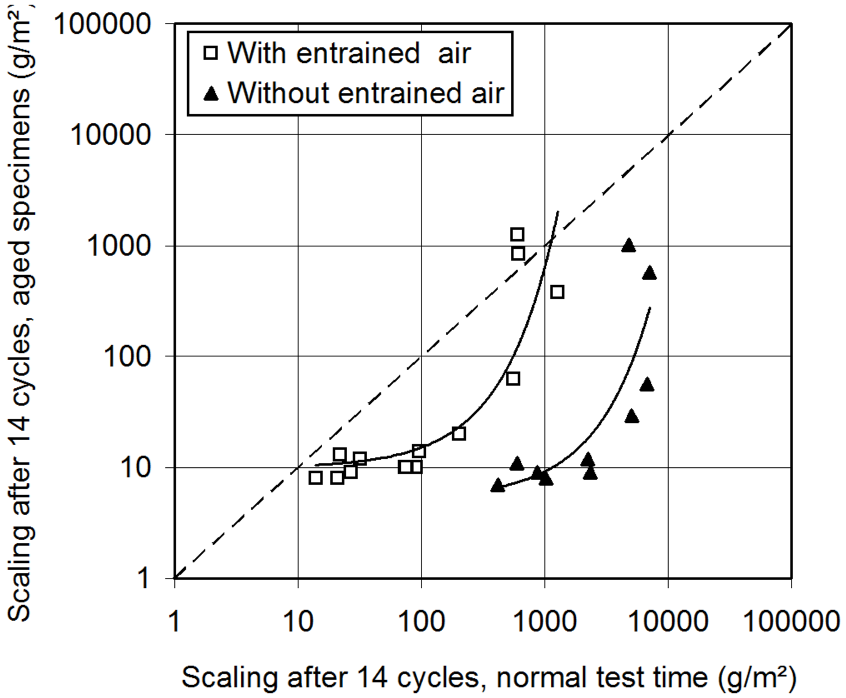

*Figure 4 – Relationship between the accumulated scaling after 14 freeze/thaw cycles for aged concrete (three years in a marine climate) and for concrete tested at an age of 28 days (normal test time). From [19].*

Results presented in [20] confirm that the properties of the concrete skin have a marked effect on the scaling resistance. It is also shown that the conditioning climate influences the scaling resistance, Figure 5.

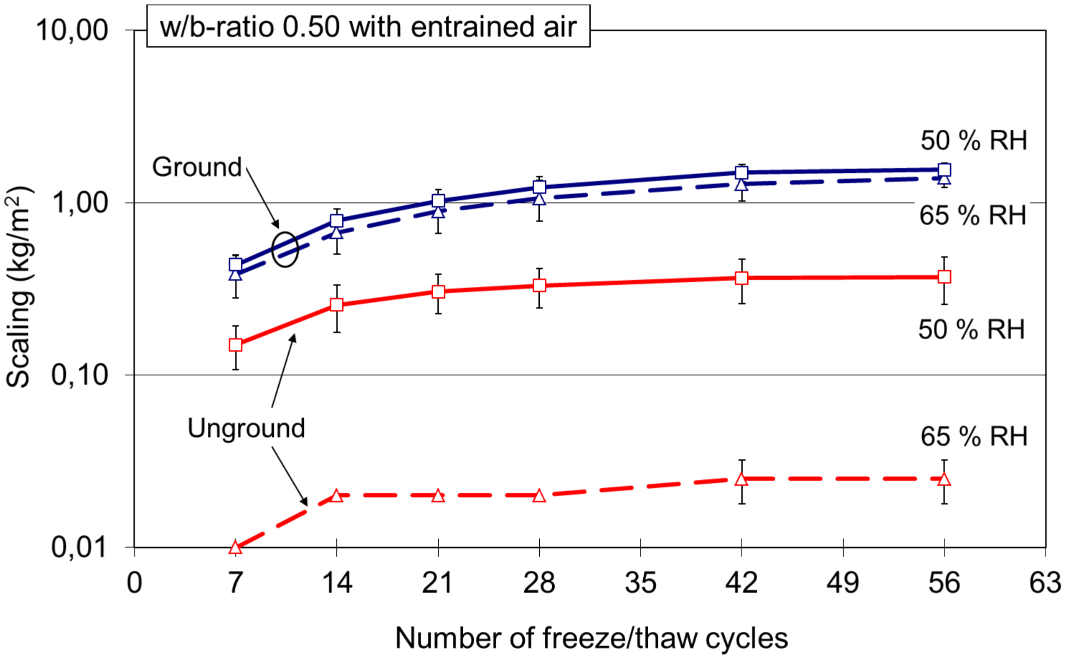

*Figure 5 – Scaling as a function of the number of freeze/thaw cycles for concrete specimens conditioned in two different climates before test start at an age of 28 days. Ground and unground test surfaces. From [20].*

Figure 5 presents scaling results for a concrete with CEM I as binder, with a w/b-ratio of 0.50 and with entrained air. Concrete specimens were treated according to the ‘slab test’ and cut at an age of 21 days. After cutting, specimens were stored in two different climates, both at 20ºC but with different relative humidities, 50% and 65%. After 7 days’ conditioning, some specimens were ground so that the uppermost half millimetre was ground off before resaturation and start of the freeze/thaw test. The results presented in Figure 5 show that for unground concrete conditioned in a climate with 65% RH, the scaling resistance is markedly better than it is for concrete conditioned in a climate with 50% RH. However, if for the same concrete the concrete surface is ground just before resaturation, the amount of scaling becomes much higher and about the same, irrespective of conditioning climate. This shows that the scaling resistance is determined by the properties of a thin surface skin and that the preconditioning climate influences these properties.

During a preconditioning period of length 7 days, as was the case in the example above, drying and carbonation ought to be the ageing parameters that influence the properties of the surface skin. For the example given in Figure 4 (ageing for three years), hydration could also be an ageing parameter influencing the properties of the concrete surface. However, results presented in [3] show that hydration has a relatively limited effect on the amount of scaling, at least for concrete older than 28 days, in comparison to the effect of carbonation. Figure 6 presents results from an investigation in which the effect of drying and carbonation during a preconditioning period of 7 days on the scaling resistance was investigated. Figure 6a presents results for a micro-concrete (aggregate up to 8 mm) with CEM I, a w/b-ratio of 0.45 and with entrained air. Figure 6b presents results for micro-concrete with 35% CEM I and 65% slag, a w/b-ratio of 0.45 and no air entrainment. For detailed information about the concrete and part materials see [3]. Three conditioning climates were investigated: 1. Specimens conditioned in water until test start, i.e. the test surface was never in contact with air before resaturation and start of the freeze/thaw test, 2. Specimens conditioned in air at 20ºC and 65% RH and a climate without carbon dioxide (filtered air) for 7 days before resaturation and start of the freeze/thaw test, and 3. Same as 2, but with a somewhat increased carbon dioxide content (1% by volume) in the climate during the 7-day conditioning period.

Figure 6 shows that there is a marked effect of carbonation on the amount of scaling for both the concrete quality with CEM I alone as binder and for the quality with 35% CEM I + 65% slag as part of the binder. However, the effect of carbonation is totally different, depending on the binder type. For concrete with only CEM I as the binder, carbonation leads to a strong reduction in scaled-off material, i.e. to an *improved* scaling resistance. The opposite applies for concrete with high slag content, with a strong increase in the amount of scaled-off material as a result of carbonation. Carbonation of concrete with high slag content thus leads to *poorer* scaling resistance. It can be noted that, the scaling is very severe during the first 14 cycles for concrete with slag, after which the rate of scaling becomes about the same as for uncarbonated material. The higher initial scaling is a result of the fact that the carbonated layer is scaled off during the initial part of the test.

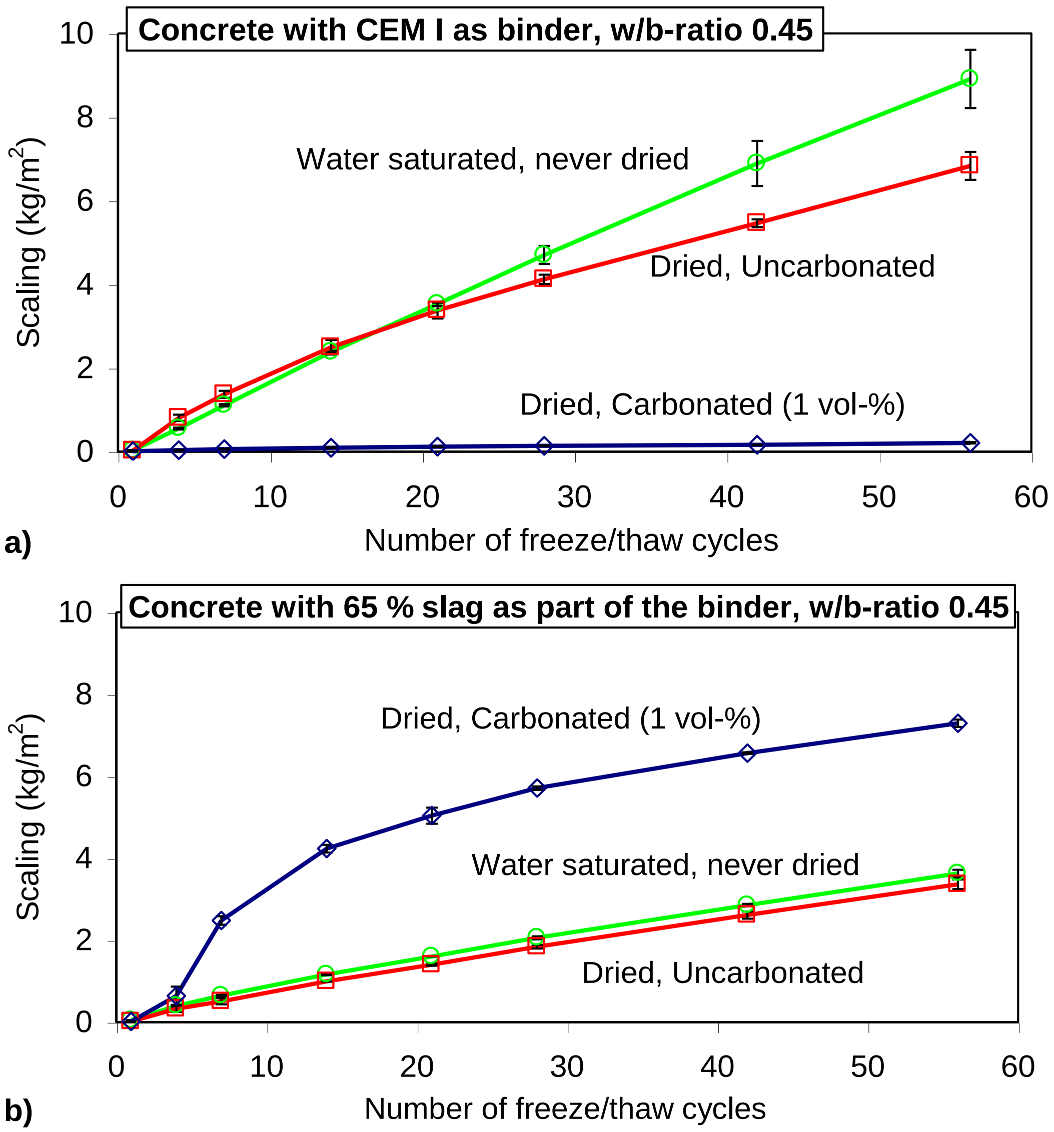

*Figure 6 – Scaling as a function of the number of freeze/thaw cycles for concrete with a w/b-ratio of 0.45 with different binders and conditioned in three different ways. a) CEM I, b) 35% CEM I + 65% slag. From [3].*

For both materials, it can be seen from Figure 6 that the effect of drying is very small compared to the effect of carbonation, i.e. the specimens dried in air without carbon dioxide show about the same amount of scaling as the water-cured, never-dried specimens. From these results it is clear that carbonation is the most dominant ageing effect.

In [3] an investigation into the effect of carbonation on the scaling resistance is presented. It is shown that carbonation leads to a change in pore structure, and thus also a change in the freezable water content. Figure 7 shows an example of the change in freezable water content as a result of carbonation for carbonated and uncarbonated mortar with CEM I alone as the binder or with 35% CEM I + 65% slag as part of the binder, both with a w/b-ratio of 0.45. The freezable water content was measured on capillary-saturated specimens during freezing, using low-temperature calorimetry. More information about material data and measurement techniques are found in [3].

From Figure 7, it can be seen that, for mortar with only CEM I as the binder, carbonation leads to a substantial reduction in freezable water content. This reduction in freezable water content presumably leads to a higher frost and salt-frost resistance for this material with CEM I alone as the binder.

For mortar with high slag content in the binder, the effect of carbonation is the opposite, i.e. carbonation leads to a substantial increase in freezable water content, at least in the temperature range down to about –40°C. This increase in freezable water content presumably leads to a lower frost and salt-frost resistance.

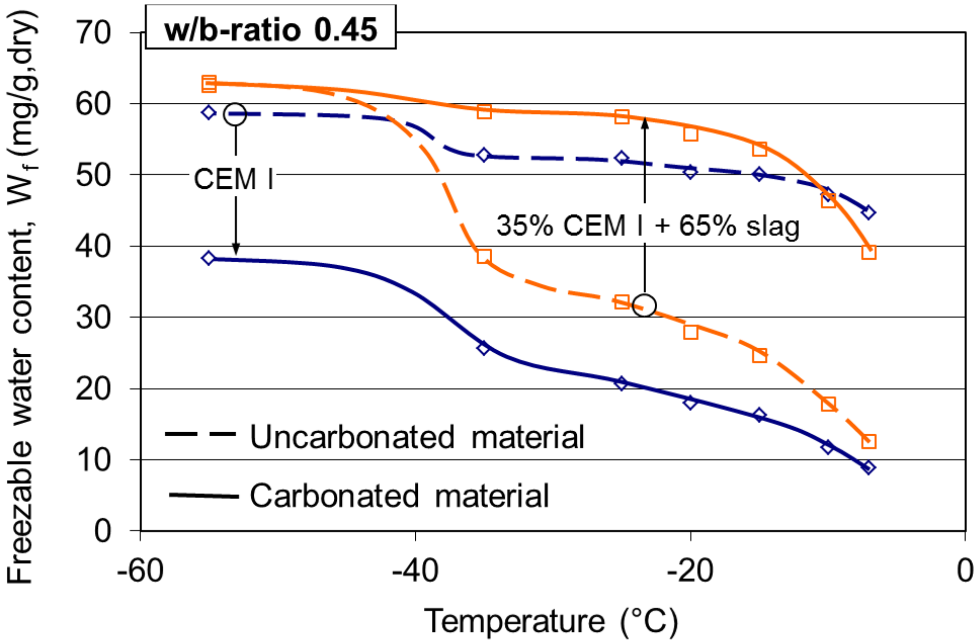

*Figure 7 – Freezable water content during freezing for uncarbonated (dashed lines) and carbonated (full lines) material of mortar with only CEM I, and with 35% CEM I + 65% slag as part of the binder, both with a w/b-ratio of 0.45. From [3].*

Another example, from the same type of measurement of freezable water content but for uncarbonated and carbonated mortar with 5% silica as part of the binder, and with a w/b-ratio of 0.45, is shown in Figure 8. The figure also shows the results for mortar with OPC alone as the binder.

Figure 8 shows that, for uncarbonated material, there is a marked difference in freezable water content, depending on whether silica is part of the binder or not. Uncarbonated mortar with 5% silica in the binder has a markedly lower freezable water content than uncarbonated mortar with OPC alone as the binder has. The effect of carbonation, however, is that both mortars have about the same freezable water content, indicating an increase in scaling resistance.

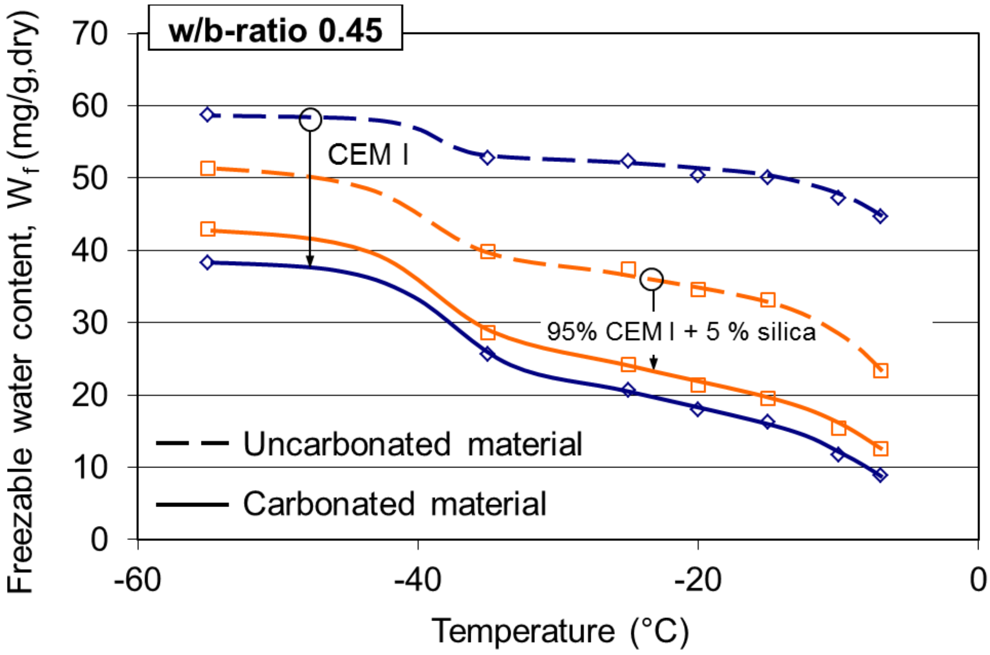

*Figure 8 – Freezable water content during freezing for uncarbonated (dashed lines) and carbonated (full lines) material of mortar with CEM I alone and with 95% CEM I + 5% silica as part of the binder, both with a w/b-ratio of 0.45. From [3].*

As can be seen from the discussion above, ageing and, in particular, carbonation influence the scaling resistance of concrete. The effects are, however different for concrete with different binder types/combinations. This has implications on how to test and evaluate scaling resistance using laboratory test methods. Today, according to the reference method in the European technical specification CEN/TS 12390-9 [1], the test surface is conditioned in normal laboratory air for only 7 days before resaturation and start of the freeze/thaw test. For concrete produced with a binder type/combination that will show poorer scaling resistance as a result of carbonation, 7 days conditioning may be too short to evaluate the long-term behaviour. On the other hand, 7 days may also be too short for concrete produced with binder types/combinations that gain scaling resistance as a result of carbonation. This needs to be studied further.

It is important that the technical specification [1] is revised so that the effect of carbonation is better taken into account. Three suggestions are presented here:

1. Conditioning that results in a deeper carbonated zone of the test surface should be used. This can be achieved by longer preconditioning times in normal laboratory air or a small increase in the carbon dioxide content in the air during conditioning. Which of these alternatives gives the most reliable results and which gives the best correlation with field experience needs to be investigated.
2. The carbon dioxide content in the climate chamber/room during conditioning should be measured and recorded. There is currently no such requirement. Different climate chambers/rooms may result in different amounts of carbonation because of different levels of carbon dioxide content. For example, the amount of fresh air versus recirculated air in the climate chamber/room influences the carbon dioxide content in the air.

3. The relative humidity in the air during conditioning should be fixed at 65 ± 5%. This is currently optional, as long as the evaporation is within 45 ± 15 g/($m^2$ h). However, also the relative humidity influences the scaling resistance, see, for example, Figure 5.

## 6. CONCLUSIONS

The following conclusions can be drawn after fourteen years' exposure at the field exposure site in a highway environment:

- Concrete with CEM I, CEM II/A-LL, CEM II A/V, CEM II A/V + 3.8% silica and CEM I + 5 % silica as binder, with entrained air and a water/binder ratio of 0.5 or below, has good resistance to internal and external damage. Concrete with CEM I + 30% slag in general also shows good resistance to internal and external damage, but the quality with a w/b-ratio of 0.50, with entrained air, shows somewhat more damage than concrete with CEM I as binder. Concrete with CEM II/A-S, in general, also shows good resistance to external damage, but there are indications of internal damage for this binder type. This needs to be investigated further in future measurements. Concrete with CEM III, however, suffers from severe scaling, even with a w/b-ratio below 0.5 and with entrained air.
- In general, internal damage is observed only for concrete qualities without entrained air and, furthermore, in most cases for concrete qualities with high water/binder ratios. However, for concrete qualities with CEM I + 5% silica as binder, internal damage is found at lower w/b-ratios, down to w/b 0.4. Further, there are indications of internal damage for concrete with CEM II/A-S, even for concrete with entrained air and with a low w/b-ratio.
- Comparing results from laboratory testing in accordance with SS 13 72 44 (the 'Slab test', essentially in accordance with CEN/TS 12390-9) with results after fourteen years' exposure at the highway exposure site shows that the laboratory standard classifies most concrete qualities correctly. Some concrete qualities with w/b-ratios of 0.50 or below and without air show only low levels of damage in the field, indicating that the slab test gives results on the safe side for these qualities, at least when compared to field experience after fourteen years. Field results for two concrete qualities containing medium to high contents of slag as part of the binder indicate more damage than could be expected from the slab test results.
- Carbonation influences the scaling resistance of concrete, and it does so differently for different binder types/combinations. For concrete with CEM I, carbonation leads to improved scaling resistance. For concrete with high contents of slag, carbonation leads to poorer scaling resistance.
- The effect of carbonation on scaling resistance is not fully considered in the current version of the European technical specification for scaling resistance, CEN/TS 12390-9. We suggest that the specification should be revised so that the effect of carbonation is better taken into account. Possible revisions include:
    - Changing the conditioning procedure to give a deeper carbonated surface zone
    - Measuring and recording the carbon dioxide content in the air in the climate chamber/room during conditioning
    - Fixing the relative humidity in the air during conditioning at 65 ± 5%.

## 7. ACKNOWLEDGEMENTS

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# Predicting AEA dosage by Foam Index and Adsorption on Fly Ash

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## Abstract

The unpredictable air entrainment in fly ash concrete caused by carbon in fly ash was studied by measuring adsorption of Air Entraining Agents (AEA) on the fly ash and by Foam Index (FI) testing. The FI test measures the mass ratio of AEA/binder required to obtain stable foam when shaking a mixture of water, binder powder and AEA, while increasing AEA-dosage stepwise. A review of concrete air entrainment and new studies combining adsorption (TGA, NMR) of AEA on fly ash with various FI test procedures, including time dependent effects on foam stability, are presented. Inter-laboratory correlation between FI and concrete air void content verifies that FI is reliable for assessing compatible binder-admixture combinations. Our adsorption- and FI measurements showed that AEA with detectable adsorption required more AEA to foam than AEA that did not adsorb on the fly ash. Foam stability was more time dependent for adsorbing AEA. NMR showed signs of chemical changes of the AEA-FA mix after adsorption.

**Key words:** AEA, fly ash, carbon, air entrainment, adsorption, foam index

# 1. INTRODUCTION

Air voids can protect concrete against frost and salt scaling damage by being places of escape for frost-induced flow and unrestrained ice formation and by reducing the degree of saturation (Powers, Helmuth 1949, 1953, Fagerlund 1971). The increased thermal contraction as air-entrained concrete freezes, compared to freezing less or non-air entrained concrete, reduces thermal incompatibility between concrete and ice and thus avoids the glue-spall induced salt scaling (Scherer et al. 2005 a,b,c, 2007). The increased contraction results from suction in the mespores created by ice in the air voids (cryosuction). The air-entrained concrete contracts so much when it freezes that there is less mismatch with the thermal expansion coefficient of ice, so salt scaling (which results from cracking of the ice) is reduced (Sun & Scherer 2010). The propagation of ice from air void to paste may also be affected by air void shell quality (Scherer 2011). This depends on w/b, the binder and the admixtures used. However, air voids cannot help to avoid frost and salt scaling damage in insufficiently cured concrete, over-saturated concrete, concrete with damaged pore structure due to heat curing, deleterious ageing effects etc.

In fly ash concrete, air entrainment has been reported to work as protection against frost and salt scaling in a number of studies (Bilodeau &Malhotra 1993, Malhotra and Ramezanianpour 1994, Jacobsen & Lahus 2001). In many experimental results FA concretes were found to be as frost durable as OPC concrete when certain limitations were imposed on w/b, FA/b, curing and air voids. Salt scaling durability was found to be a bit more variable than frost durability. A negative effect of slow curing on frost and salt scaling, as well as difficulties with obtaining good air-void systems in fly ash concrete, were recognized.

Problems with air entrainment in fly ash concrete have mainly been attributed to variable Loss on Ignition (LOI) in the fly ash, presumably due to (unburned) carbon (Gebler& Klieger 1983) interacting with the AEA. The Foam Index (FI) test has been used as a fast way of testing the effect of different binder-admixture combinations on air entrainment and can be useful if the fly ash is suspected of causing variable air entrainment.

This paper reviews air entrainment with focus on fly ash and experiences with FI on various fly ashes and its relation to concrete air entrainment. New studies on adsorption and characterization of AEA adsorbed on fly ash combined with Foam Index measurements are presented to help obtaining reliable and predictable air entrainment in fly ash concrete.

# 2. AIR ENTRAINMENT AND FOAM INDEX

## 2.1 AEA and some factors affecting air content in concrete

Air entraining agents (AEA) can be described as mixtures of various surfactants. Manufacturers often provide more or less unenlightening descriptions, such as vinsol resin, tall oil, and synthetic tensides. In (Dodson 1990, Rixom 1986, Du & Folliard 2005) AEA are described as having hydrophilic (anionic, cationic and non-ionic) «heads» oriented toward the liquid and hydrophobic hydrocarbon chain «tails» oriented toward the air in the void. Their function is described as reducing water-air surface tension, adsorbing to solid surfaces and stabilizing air bubbles in fresh concrete. The distribution of AEA in fresh concrete proposed by Du and Folliard (2005) is:

$$AEA_{\text{added}} = AEA_{\text{interface}} + AEA_{\text{adsorbed on solid}} + AEA_{\text{liquid}} \qquad (1)$$

This is over-simplified, as it neglects the kinetics of adsorption, which leads to exchange of molecules between the terms on the right side of the equation.

After the formation of air bubbles, they may disappear, change or collapse in fresh concrete due to migration to the surface, diffusion of air from small to large bubbles, dissolution of air from bubbles into liquid, and coalescence of two or more bubbles due to capillary flow (drainage) between bubbles (Fagerlund 1990, Du & Folliard 2005). Fagerlund (1990) calculated that air bubbles with diameters below 20 – 40 microns in fresh paste of w/c = 0.50 can dissolve in the water around the void. Dissolution occurs because the higher air pressure ($p = 2\gamma/r$) generated by the surface tension, $\gamma$, in voids with smaller radius, $r$, enhances the solubility of air in water. The water becomes saturated with air as the small voids dissolve, so the air diffuses to the larger voids causing them to expand, resulting in increased total air volume. Both the dissolution of air and the diffusion of air from small to large bubbles depend on several factors, including the volume fraction of water in the fresh paste and tightness of the air void wall (Fagerlund 1990, Gutman 1988). Fagerlund estimates that a 10 µm bubble could dissolve in 10-30 minutes. He also notes that the AEA and other organic additives encourage formation of smaller air bubbles, so the changes in the distribution during the induction period could be substantial.

Change and disappearance of air voids might also be due to other mechanisms related to foaming and forces acting in solid-liquid-gas emulsions: lifting (buoyancy, momentum) and downward resistance (drag, surface tension, particle-bubble collisions) (Yang et al. 2007). This implies that rheology of fresh concrete also plays a role in the movement and viscous drag on air voids due to the rate of shear of the fresh concrete. Thus, in practice air entrainment consists of several effects acting concurrently with the stabilizing effect of AEA.

Air content increases in more or less the same way with increasing AEA dosage for pure paste (binder, water, admixture), concrete and mortar (Joliceur et al. 2003). However, the entrained air volume is much higher in mortar than in concrete, whereas pure paste gets lower air entrainment than mortar and concrete for a given AEA dosage (Joliceur et al. 2003, Hammer and Johansen 2005). This even holds when comparing air void content by paste volume fraction, so apparently aggregate affects air entrainment. Capture of fine air voids in the paste between fine sand particles in the fraction 0.3 – 0.6 mm is suggested (Rixom 1986). According to Geiker & Kjær (1995) the air voids captured between the fine sand particles (0.15 – 0.6 mm) are the ones stabilized by AEA, thus affecting air pore structure. Crushed aggregate might disperse air better than natural gravel (Rixom 1986, Du & Folliard 2005). However, increased content of fines smaller than ~20 microns reduces air, as the fines in pozzolans do (Rixom 1986).

A few other rules of thumb for varying air volume in fresh concrete are found in the literature. Increased temperature reduces air content. This is probably mainly owing to less available AEA due to adsorption on hydration products and also complex chemical-physical mechanisms related to reaction, coagulation and precipitation of AEA that reduce the air entraining effect with increased temperature (Du & Folliard 2005, Rixom 1986 p.107,117, Dodson 1990 p.135,137). Thus the physical effects of reduced solubility of air in water and increased pressure in air at increased temperature do not seem to relate to change of concrete air content at increasing temperature. Prolonged mixing (> 5 – 10 min) reduces air content (Rixom 1986).

The effect of rest, transport, pumping/distribution, placement compaction and pressure can be assumed to reduce fresh air content, depending on the stability of the air void system (Geiker & Rostam 1995, Du & Folliard 2005). Contradictory reports on the effect of pumping on air void content exist. Traditional plastic consistency concrete with 320 kg/m$^3$ was reported to have increased air-void content after pumping (Johansson & Tuutti 1976). Concrete with superplasticizer is more easily air entrained than concrete with less flow, but is also more susceptible to loss of this air during pumping (Kaplan 2001, Spiratos et al. (2003) p.110). Highly flowable concrete with superplasticizer, including HPC concrete, showed reduced air content in hardened concrete after pumping in several studies. Air voids less than ~50 microns were found most susceptible to disappear, more so after vertical than after horizontal pumping (Pleau, Pigeon, Lamontagne, Lessard 1995). Geiker and Rostam (1995) studied air content and air void structure in 17 different mixes as function of pumping and pumping conditions. They found reduced total air content, reduced content of voids < 0.35 mm, and increased spacing factor after pumping in practically all tests. Prolonged time under pressure was found to have an extra effect on reducing air content. Furthermore, their tests included comparable concrete mixes with OPC and OPC+fly ash, but no clear difference in loss of air voids could be discerned. Pleau et al. (1998) found that the air void structure may not necessarily be completely destroyed by job-site pumping, since the number of very small voids that contribute most effectively per unit volume to spacing and surface was still very high after pumping. The spacing factor in hardened w/c = 0.43 concrete (100 mm slump) increased from 0.18-0.20 mm before to 0.22-0.31 mm after pumping. For w/c = 0.30 concrete (200 mm slump) a much larger increase in spacing factor in hardened concrete was found in the same study: from 0.18-0.22 mm before to 0.43-0.49 mm after pumping. Lepage et al. (1998) investigated pumpability and effect of pumping on air void structure in w/b = 0.38 (70-90 mm slump) and w/b = 0.30 (110-210 mm slump) concretes with hydroxycarboxylic acid water reducer and fatty acid based AEA. Air void spacing in hardened concrete was less affected by pumping for the w/b = 0.38 concrete (0.12 – 0.13 mm before and 0.14-0.16 mm after pumping) whereas the w/b = 0.30 concrete had more serious damage to its air void system by the pumping (0.18-0.23 mm before and 0.42-0.49 mm after pumping). Jensen, Hasholt and Geiker (2005) studied the air void stability in SCC as affected by formwork pressure during curing. They found that Boyle-Mariottes law applies for prediction of air content in pressurized fresh concrete. A fair prediction of increased spacing and reduced specific surface in hardened concrete could be made assuming equal pressure on all voids with the standard equation for Powers spacing factor. Full scale pumping tests showed that pumping from bottom was more destructive to the air void structure than pumping from top.

Thus the void spacing is most increased by pumping in highly flowable concrete by increased pressure, particularly at form filling from below. Prolonged pressurization time further reduces the air content and increases the spacing. An effect of fly ash on loss of air during pumping has not been observed.

## 2.2 AEA dosage and stability with fly ash, silica and different OPC cements

Generally, an increased AEA dosage is needed when adding pozzolans, such as fly ash (Malhotra and Rameizanpour 1994) and silica fume (Sellevold and Nilsen 1986), to maintain a constant air void content. Presumably the increased specific surface of the binder plays a role. In fresh silica fume concrete, a higher stability of the entrained air was found compared to OPC-concrete (Sellevold and Nilsen 1986) and compared to FA-concrete (Geiker & Kjær 1995). Increased cement fineness also reduces air content, or increases necessary AEA dosage to obtain a given air content, whereas increased cement alkali content increases entrained air (Dodson 1990, Du & Folliard 2005).

The effect of fly ash on the stability of air void content in fresh concrete seems to be less known, except for all the problems reported related to variable carbon content of the fly ash mentioned in Section 1. In general, the effect of increased LOI or carbon content is to reduce air content (or to increase the necessary AEA dosage). The reason for this is presumably that the carbon adsorbs AEA, owing to its high surface area and/or strong chemical affinity, thereby reducing available AEA and thus air entrainment (Gebler and Klieger 1983). The approach proposed to solve this issue has been to increase the AEA dosage or switch to a product that works, mainly on an empirical basis. The difficulties in predicting the effect of air entrainment also includes effects of the many possible combinations of admixtures, binders, concrete mixes and practical circumstances.

## 2.3 Foam Index and air content in concrete at varying LOI and/or carbon content

*Foam Index testing*

The foam index (FI) test was originally developed by Dodson (1990) to test the effect of variation of Portland cement characteristics (specific surface, alkali content) on air void formation in concrete. It has been used to assess the effect of fly ash on air-void formation (Gebler and Klieger 1983, Baltrus et al. 2001, Külaots 2003, Vestgarden 2006, Harris et al. 2008a,b,c, Ollendorff 2011). The FI test, in brief, consists of shaking a mixture of water and binder powder (typically w/b = 2 – 2.5), and increasing the AEA dosage stepwise until stable foam forms on top. We use an automated Griffin flask shaker with 2.4 Hz frequency and modified with an arm giving 20 mm amplitude to agitate a plexiglass container with 70 ml volume and 40 mm inner diameter; shaking for 60 seconds is used to mix water and binder, and then 15 seconds shaking with AEA. The stability of the foam forming on top of the slurry is then observed while at rest for 45 seconds. If the surface does not remain covered with stable foam, the AEA dosage is increased with a pipette, then shaking for 15 seconds and observation for 45 seconds is repeated until stable foam covers the surface. The FI is then simply the concentration of AEA in ml/kg binder when the foam remains stable.

Figure 1 shows the results of FI testing of 3 different low-lime fly ashes (1.0, 3.1 and 3.9 % carbon with Blaine surface area of 357-359 $m^2/kg$) from Europe provided by Norcem, a Norwegian Norcem CEM I 52.5 OPC with Blaine = 360 $m^2/kg$, and one test on pure water (Ollendorff 2011). The air entraining agent was Sika Aer-S which is described as “synthetic tenside” according to the product sheet. The test with only 25 ml of deionized water had ≤ 5% lower filling than the tests with w/b = 2.5 slurries, due to absence of binder volume (~3 ml). Each curve is the mean of 3 parallel samples except for the OPC, where 6 parallel samples were used. Scatter was lowest for low carbon FA (Coefficient of Variation = 1 %), a bit higher for water and OPC (CV = 4 %) and highest for high carbon FA (CV = 8 and 12 % for 3.1 and 3.9 % carbon respectively).

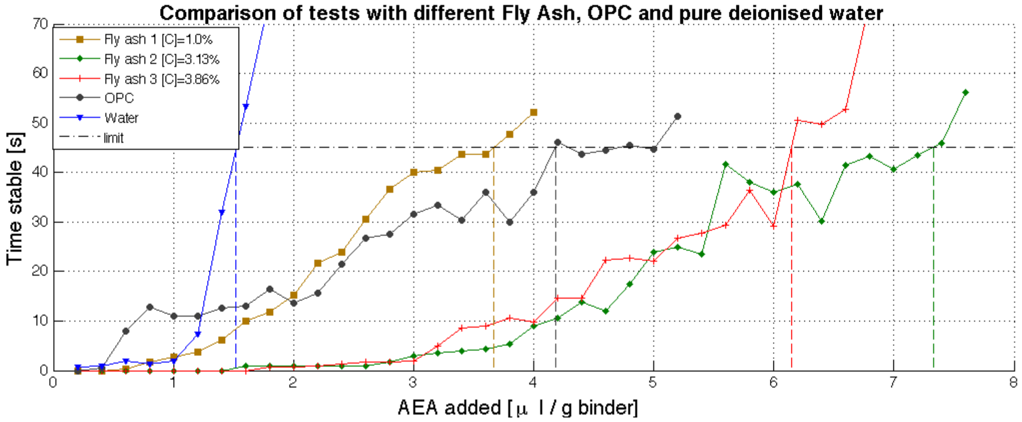

*Figure 1 – Foam Index (µL/g) of 3 fly ashes, 1 OPC CEM I 52.5 and only deionized water (Ollendorff 2011)*

Figure 1 shows that AEA and pure water foams easily in the shaker at very low AEA dosage. The AEA dosage with only water is calculated per 2.5 g of water. A much higher AEA dosage was required to obtain foam when introducing powder particles. The low-carbon fly ash and the pure cement each showed rather low, and similar, FI. That is, these two types of particles had approximately the same effect on foaming. The two high-carbon fly ashes had higher FI, as expected. The recommended normal dosage of this AEA in concrete is 0.01 – 0.08 % of cement weight = 0.1 – 0.8 µL/g which is only in the order of 2 – 20 % of the dosage required for stable foaming in the FI-test. This difference can be due to different mechanisms of air entrainment in concrete (stabilization) than in the FI-test (foaming). However, as we shall see, experience shows a correlation between FI and air entrainment in concrete.

In Tables 1 and 2, compilations of various foam index test results on different fly ash binders and AEA are shown. Table 1 show that the FI test conditions applied by the different authors vary with respect to drop size, AEA dilution, sample- and container size. In addition the shaking was often done manually, thus probably varying somewhat between the tests. Harris et al. (2008a,b,c) proposed a standardized FI test based on experience with different FI test procedures on 4 different fly ashes. In their tests, the coefficient of variation went up to 20 % when doing 3 parallel FI tests on each type of ash with 4 different FI test procedures, of which only the results of the procedure correlating best to concrete air void content is shown in Tables 1 and 2.

Figure 2 shows the evolution of foam during the standard test for the high carbon ash shown in Figure 1. Figure 3 shows the different structures of stable foams on the 3 ashes in Figure 1. It is seen that the nature and structure of the foam varies (bubble size, foam volume) both during propagation, as the foam gradually fills the surface before the test end point, and as stable foam is reached (Ollendorff 2011).

*Table 1 - Test conditions in FI tests*

| Reference | w/b | AEA dilution | Drop size µL | Shake sec. | Rest sec. | Volume container mL | Binder g |
|---|---|---|---|---|---|---|---|
| G&K | 2.5 | 1:43 | ? | 15 | 45 | 473 | 20 |
| Baltrus | 2.5 | 1:40 | 50 | 15 | 15 | 15 | 2 |
| Külaots | 2.5 | 1:9 | 20 | 15 | 45 | 70 | 10 |
| Vestgarden | 2.5 | 1:9 | 20 | 15 | 45 | 70 | 10 |
| Harris bottle | 2.5 | 1:19 | 10 | 15 | 45 | 132 | 10 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Ollendorff | 2.5 | 1:9 | 20 | 15 | 45 | 70 | 10 |

*Figure 2 – Evolution of foaming in 40 mm diamter FI test container of high Carbon fly ash in figure 1 (Ollendorff 2011)*

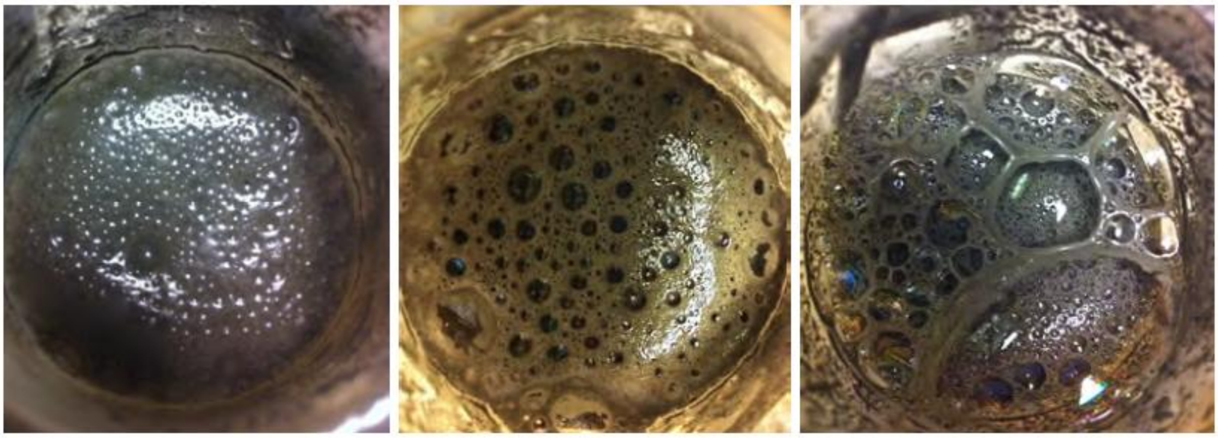

*Figure 3 – Varying foam structures at stable foaming of (from left) ash No. 3, 2 and 1 in figure 1 (Ollendorff 2011)*

Table 2 shows a selection of data from (Gebler and Klieger 1983, Baltrus et al. 2001, Külaots 2003, Vestgarden 2006, Harris et al 2008a,b,c) together with the new results (Ollendorff 2011). Within each of these studies it was found that the AEA dosage needed to obtain stable foam increases with increasing carbon content and/or increasing loss on ignition of the fly ash. Comparison should preferably be done within the same series of tests due to the different procedures. Furthermore it is not clear from the data whether carbon or loss on ignition is best related to FI.

*Table 2 - Foam index for combinations of AEA and fly ash binders with varying LOI*

| Ref | AEA | Binder | Carbon<br>% of mass | LOI<br>% of mass | FI<br>µl/g binder |
|---|---|---|---|---|---|
| G&K | Vins.Res. | 80%OPC+20%FA | 0.1/1.2/4.2 | 0.4/1.8/4.9 | 4.5/6.5/12 |
| Baltrus | Darex 2 | FA | 0.3/4.0/14.6 | - | 50/24/66 |
| Kulaots | Darex2<br>Air 40 | 80%OPC+20%FA | - | 6.1<br>66/21 | 15<br>133/60 |
| Vestgarden | Micrair100 Fatty acid | 1 SR OPC, 9 different 20%FA | *-3.8 | 1.4-4.7 | 11-47 |
| Harris et al | Wood Rosin | 80%OPC+20%FA | - | 0.8/0.4/0.1/0.6 | 10/7/6/3 |
| Ollendorff (Fig.1) | Sika Aer-s synt.tens. | OPC, FA or only water | **/1/3.1/3.9 | 2.5/1.1/3.6/4.5 | 4.2/3.7/7.3/6.2 |

*, **: not measured (sulphate resistant low-$C_3A$ OPC, OPC)

*Relation Foam Index – air content in concrete*

The usefulness of the FI test depends, of course, on its ability to predict air content in concrete. Measurements of air content in fresh concrete made with the same ash and AEA as in the FI test, however, were only published in a few cases (Gebler & Klieger 1983, Vestgarden 2006, Harris et al. 2008). FI was correlated to air content or AEA dosage in concrete in various ways for different types of AEA and fly ashes.

Gebler and Klieger (1983) used constant concrete consistency and air content at variable AEA concentration and w/b = 0.40-0.48 (Vinsol resin and no Water Reducing Agent (WRA)) with different ashes. The concrete mixes were carefully made without water reducer to obtain 6 ± 1 % air by varying the Neutralized Vinsol Resin AEA dosage and adjusting w/b so that slump varied between 3 and 4 inches (~75 - 100 mm). The correlation between FI and AEA dosage for 6 % air in a linear plot was $R^2$= 0.93 for 10 ashes /1 OPC reference.

Figure 4 shows a plot of FI versus air content in fresh concrete, based on the data by Vestgarden (2006). He used constant dosage of AEA (0.18 kg/$m^3$ of fatty acid polyglycol type AEA and polycarboxylate high range WRA (= Super Plasticizer - SP[1]) in a constant concrete composition of w/b = 0.41 with 10 different ashes and 1 control mix. All mixes had 2.4 kg of co-polymeric water reducer and 420 kg binder (20 % FA, 5 % SF and one reference without FA). The slump immediately after mixing varied in the range 165 – 225 mm. The correlation between FI (our automated shaker) and fresh air void content after 10 minutes in a power function was $R^2$ = 0.84 for 9 ashes/1 OPC reference.

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[1] The term SP is used in Europe while High Range WRA is used in North America.

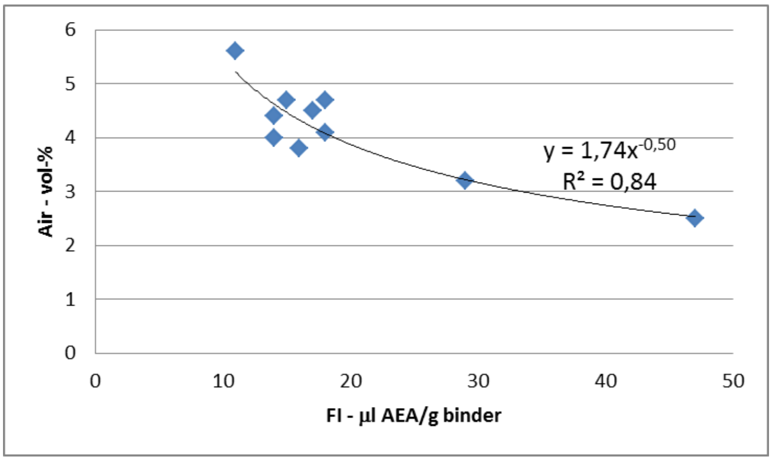

*Figure 4 - FI vs air content in fresh concrete after 10 minutes (Vestgarden (2006))*

In the study by Harris et al. (2008a,b,c), AEA was added to obtain constant concrete air-void content of 6.0 % at constant w/b = 0.45 (wood rosin type AEA and ASTM C494 type D WRA) with 4 different ashes. This work showed best correlation coefficient $R^2$ = 0.94 in a linear plot between FI (bottle-type FI test) and AEA dosage to obtain 6.0 % air in fresh concrete.

Note that in the 3 cases cited above, the FI tests were made with only AEA, binder and water, whereas in concrete two of the test series combined WRA and AEA and one of the concrete series in addition contained silica fume. Considering the wide variation in materials and test conditions, this indicates that the FI-test is useful for inter-laboratory prediction of the effect on concrete air entrainment of varying AEA-Fly ash combinations.

*Foam tests with combinations of AEA and water reducers*

The effect of combinations of AEA and WRA on air entrainment can be difficult to predict. According to Rixom (1986) lignosulphonate and hydrocarboxylic AEA work with WRA, and also alkyl-sulphate AEA can work with WRA. Pre-screening tests of admixtures include foam stability tests, in addition to FI tests. While the FI uses a water/binder ratio of ~2.5 and often a similar binder composition as the concrete, foam stability measurements are made with only liquid and admixture or a w/b ratio in the order 10 – 50. These are thus even further away from concrete than the FI-test. Foam stability measurements have been used to study the chemistry of surfactants for a long time and the foaming has been correlated to surface viscosity, see for example (Brown et al. 1953, Shah et al. 1978). In the foam stability test, the aqueous solution with admixture is usually shaken in a tall glass. The foam volume gets much larger than in the FI test and the foam stability is measured over more than an hour. A variety of such foam stability tests have been used on AEA-solutions.

Studies of foaming and surface tension of mixtures of WRA and AEA and subsequent studies of air entrainment in concrete including air void structure (Eriksen & Andersen 1986) showed that melamine-type WRAs worked with both AEA based on “synthetic tenside” and on “vinsol resin”, whereas naphthalene-type WRA worked with vinsol resin. These 3 AEA-WRA combinations were the only ones that both gave good foaming and good air void systems in hardened concrete (Eriksen & Andersen 1986). The studies showed no clear relation between foaming and measurements of surface tension in the foaming solution. Based on foam stability measurements combined with microscopy observations of bubbles and freeze/thaw testing of concrete, it was claimed that bubble wall thickness is important for concrete air void stability and freeze/thaw durability (Gutman 1988). Foam meter studies of AEA with low-alkali cement containing 6 % silica fume, 12 % fly ash, and different WRA/AEA combinations, showed medium foaming and some loss of foam during 90 minutes, compared to when these admixture combinations were used with pure OPCs or pure slag (Sørensen and Geiker 1995, HPC Specification Dansk Betoninstitut 1995).

AEA and AEA-WRA combinations were studied in fresh concrete aiming to find solutions robust against variable fly ash carbon content (Nkinamubanzi et al. 2003, Vollset & Mortensvik 2011). The latter work showed that stable air pore structure can be obtained with AEA and polycarboxylate-based SP in flowing consistency concrete that was not pumped. However, both studies provide limited applicability for concrete technologists, beyond telling what brand names to choose.

Ready-mix concrete producers typically have standard solutions that work most of the time. For high slump concrete (typically 200 mm slump) co-polymer water reducing agents are usually mixed a bit before AEA is added as the final constituent to the mix. On-site problems with unstable air content are, however, common (Mørtsell, Heidelberg Cementgroup pers. comm. 2011) and robust solutions are therefore needed. Vestgarden (2006) used the FI test to assess AEA-WRA combinations and mix procedures by combining two different polycarboxylate SP with “tenside” AEA with one powder mix (75 % OPC and 25 % FA) with low/moderate carbon content, applying 4 different FI-test procedures:

- only AEA
- AEA+SP mixed in simultaneously
- SP first, then AEA
- AEA only, then adding SP “dropwise”

FI decreased somewhat when mixing AEA and the SP simultaneously (FI = 28 μL/g) compared to FI obtained with only AEA (FI = 32 μL/g). Adding SP and mixing a bit first with water and powder, and then adding AEA further reduced FI (= 24 μL/g). The fourth FI procedure, with first adding AEA, water and binder powder and producing stable foam, and then adding the SP and continuing shaking, showed less and less foam as more SP was added. Apparently this delayed SP addition caused very high effective FI. There were only minor differences, if any, in the effects of the two types of co-polymeric super plasticizers. Thus it seems that the lowest FI corresponds to the above referred mixing sequence preferred in practice.

To sum up, both type of AEA and WRA as well as the mixing transport, placement/casting and compaction affect air entrainment. More knowledge is needed to find generic materials that work together and to understand the mechanisms of air entrainment.

## 3. COMBINING AEA ADSORPTION ON FA WITH FOAM INDEX

Following the studies with TGA and NMR (Tunstall & Scherer 2011) of AEA adsorption on fly ash, Foam Index measurements were made on the same materials (Ollendorff 2011). Two fly ashes with low and high carbon contents were selected from the US market. These two ashes had 2.4 % and 11.73 % LOI and 1.7 and 6.7 $m^2/g$ BET surface areas, respectively. In addition, 4 different AEA from the US market were investigated: Saponified Rosin (SR), Synthetic Olefin Sulfonate (SOS), Saponified Tall Oil (STO) and Neutralized Vinsol Resin (NVR).

## 3.1 Adsorption measurements

A Perkin-Elmer TGA was used on various quite concentrated AEA solutions. First AEA solutions that had not been mixed with FA were run through the TGA temperature cycle to measure the residual solids content of each AEA. TGA measurements were made on the supernatant of solutions of AEA that had been exposed to fly ash and then filtered, thus giving the amount of AEA retained in the solution (i.e. not adsorbed on the FA). In addition $^1$H NMR spectra were made of selected pure AEA and AEA after mixing with varying amounts of selected Fly Ash using a Bruker Avance III NMR instrument (Tunstall & Scherer 2011).

## 3.2 Foam Index (FI) measurements

Three different foam index test procedures were run on combinations of the US Fly Ashes and AEA. The FI testing was made with the automated shaker described in section 2.3, Figure 1 and Tables 1 and 2. In addition to the “standard” procedure, “short” and “long” tests were made to investigate the effect of adsorption on foaming and foam stability (Ollendorff 2011). For all these tests two parallel samples were run.

*“Standard” FI test*
The 70 ml container with 40 mm inner diameter was filled with 10 g fly ash and 25 g distilled water and an initial 60 seconds shaking was done with 2.4 Hz frequency and 20 mm amplitude. Then one 20 μL drop of 1:9 AEA solution was added, followed by 15 seconds of shaking. If the foam was not stable after 45 seconds then another 20 μL drop of 1:9 AEA solution was added and the cycle [15 seconds shaking and 45 sec waiting while observing for stable foam] was repeated. This was done with a sufficient number of AEA drops to obtain stable foam. FI was calculated as μL AEA/g binder when stable foam was observed, as shown in Figure 2.

*“Short time” FI test*
In this FI test, half the amount of AEA determined in the “standard” FI test was added after 60 seconds of initial mixing. Then the mix was shaken for 15 seconds and observed for 45 seconds to determine foam stability. If necessary, the procedure [a 20 μL drop of AEA solution added, 15 seconds of shaking and 45 sec waiting] was repeated until the foam remained stable.

*“Long time” FI test*
In this FI test, the sample from the “short time test” with stable foam was left with the lid on for 1 hour. Then, if the foam was still stable “Long FI” = “Short FI”. If the foam had disappeared, then one 20 μL drop of 1:9 AEA solution was added, followed by 15 seconds shaking, and 45 seconds observation. In this way, both foam stability and effect of adsorption kinetics on necessary additional amount of AEA to regain foam was determined.

## 4. RESULTS AND DICUSSION

Figures 5 and 6 show adsorption determined by TGA for concentrated Saponified Rosin (SR) and Synthetic Olefin Sulfonate (SOS) exposed to high carbon fly ash.

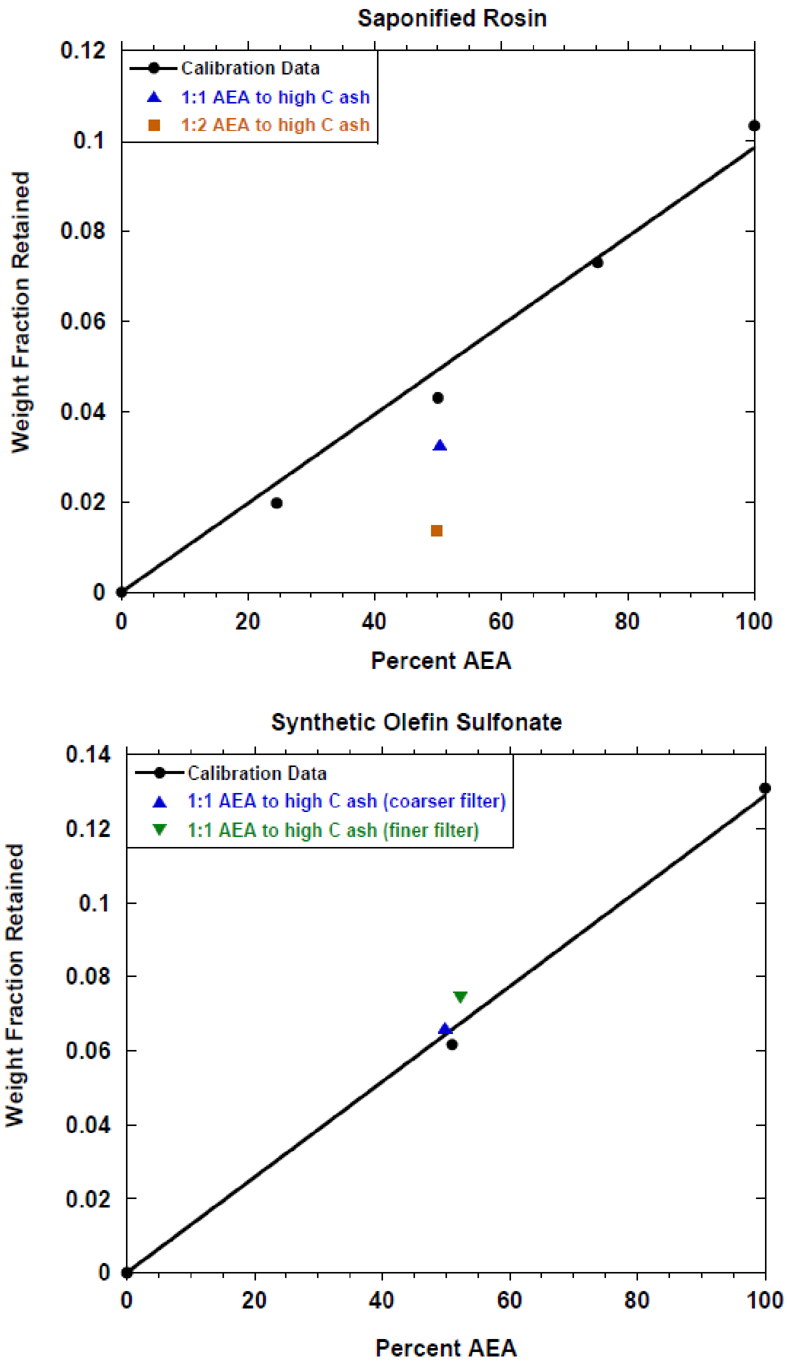

*Figure 5 – Adsorption of SR AEA (upper) and no adsorption of SOS (lower) on fly ash determined by TGA(Tunstall & Scherer 2011)*

Figure 5 shows that adsorption differed between the different types of AEA expressed as % AEA added versus residual AEA in the solution. There was detectable adsorption of Saponified Rosin, whereas there was no detectable adsorption of Synthetic Olefin Sulfonate (SOS), Saponified Tall Oil (STO), nor Neutralized Vinsol Resin (NVR) on high-carbon fly ash. Similar results as those of SOS shown in Figure 5 were thus obtained for STO and NVR.

Furthermore, the preliminary NMR studies (Tunstall & Scherer 2011) revealed a selective adsorption and/or chemical change in the AEA-FA mix of certain AEA ingredients or some other kind of interaction, as shown in Figure 6. As a simplified description, the positions of the peaks in Figure 6 represent the species present, whereas the peak sizes represent the amounts of the different species.

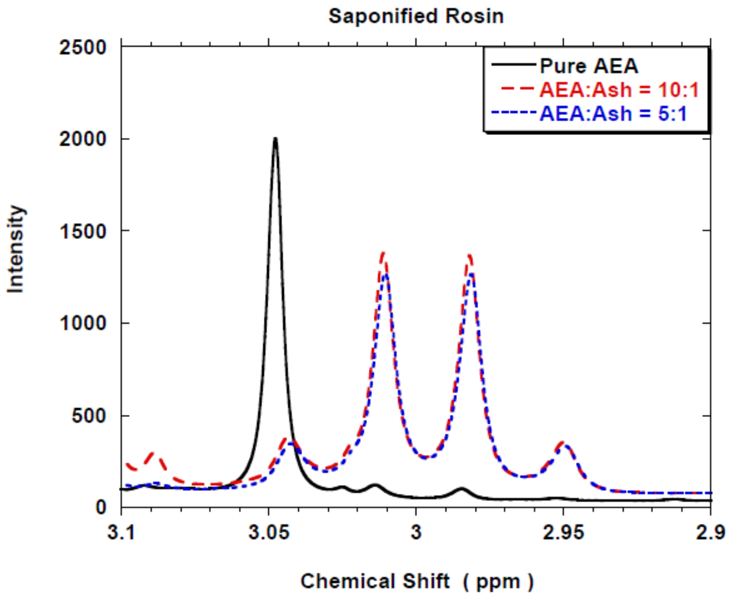

*Figure 6 – $^{1}$H NMR spectra for AEA without and with adsorption on high carbon FA (Tunstall&Scherer 2011)*

The Foam Index tests were run after the adsorption measurements. The two air entraining agents SR (adsorption) and SOS (no adsorption) that are shown in Figure 5 were selected for all three types of FI tests described in the previous section (standard, short, long) on low- and high carbon fly ash. In addition the standard FI test was run on Neutralized Vinsol Resin (NVR) with high carbon fly ash. Table 3 shows the results of the "standard" and the "short" tests whereas table 4 shows the results of the "long" test. All results are mean values of two parallel samples.

*Table 3 – Foam Index test results with "standard" and "short" procedure*

| AEA | Fly Ash | Procedure | FI (µL/g) |
|---|---|---|---|
| SR | High Carbon | Std | 193 |
| | High Carbon | Short | *104* |
| | Low Carbon | Std | 18.4 |
| | Low Carbon | Short | *17.6* |
| SOS | High Carbon | Std | 40 |
| | High Carbon | Short | **36** |
| | Low Carbon | Std | 4.8 |
| | Low Carbon | Short | **4.8** |
| NVR | High Carbon | Std | 32 |

*Table 4 – Foam Index test results with "long" procedure*

| AEA | Fly Ash | Stable time (sec) | Additional (µL/g) | FI (µL/g) |
|---|---|---|---|---|
| SR | High Carbon | 22.9 | *48* | *152* |
| SR | Low Carbon | 35 | *4.8* | *22.4* |
| SOS | High Carbon | ≥ 45 | 0 | **36** |
| SOS | Low Carbon | ≥ 45 | 0 | **4.8** |

Table 3 shows that the high carbon fly ash mixed with the adsorbing AEA (SR) gives very high FI, both in “standard” and “short” procedures. These FIs (104-193) are even higher than the highest Foam Indices among the reviewed data presented in Table 2. Table 3 also shows that the “short” procedure reduces the FI for the adsorbing AEA compared to the “standard” procedure. That is, foaming is obtained with less AEA (and lower number of repeated shaking) by adding a lot of AEA at once, instead of many small droplets over long time.

Table 4 shows that the adsorption of AEA on high-carbon ash has a time-dependent effect on foaming, since the foam disappears within an hour (i.e., bad foam stability) and additional drops of AEA are needed to regain stable foam. Table 3 shows that the low-carbon fly ash gives a much lower FI, both in the standard and short procedures with AEA SR, though FI is still a bit high compared to the lowest FI values reviewed and shown in Table 2. From Table 4, it is seen that there is a time-dependent effect for this AEA-FA combination too, since the foam was not stable for an hour, but could be regained after additional AEA was added. The increase in FI from “short” to “long” procedure due to adsorption, and the new FIs, are seen in *italics* in Tables 3 and 4. Most additional AEA is needed on the high-carbon fly ash: *48* μL/g, whereas additional *4.8* μL/g is needed on the low-carbon fly ash.

Tables 3 and 4 show that the non-adsorbing AEAs (SOS, NVR) on high-carbon fly ash have comparably low Foam Indices: 40 and 32 μL/g in the standard FI. SOS was also run in the “short” and “long” procedures and showed no time dependency, since there was little/no difference in FI. (The reduction in FI from 40 to 36 for SOS on high carbon fly ash in table 3 when going from “standard” to “short” is within the error of the experiment). Furthermore, the foam remained stable over 1 hour (see bold numbers for the non-adsorbing SOS). Finally, we see from Table 3 that the non-adsorbing SOS with the low-carbon fly ash has the lowest FI of all combinations, with FI values comparable to the lowest values in Table 2.

The time dependency of the adsorption had a clear effect on increasing the foam index, since less AEA became available for foaming. The standard procedure, with drop-wise addition and shaking at regular intervals, took 3 hours to obtain stable foam for the adsorbing SR on high carbon fly ash. This reduced to only 3 minutes to obtain stable foam in the short procedure and then increased to (60+13) minutes in the “long” procedure. For the adsorbing SR on low-carbon fly ash, the “standard” test took 12 minutes, while the “short” test took 6 minutes and then the “long” test took (60+14) minutes. Apparently, adsorption went on for quite some time, since the time to regain foam by drop-wise addition after 1 hour took 13 – 14 minutes, whereas the “short” procedure could create a lot of unstable foam when adding a lot of AEA quickly. For the non-adsorbing SOS on high-carbon fly ash, the test time was 50 minutes in the standard FI test, reducing to 5 minutes in the short test and then remaining stable for an hour (i.e., no increase of FI in the “long” test).

## 5. CONCLUSIONS

The Foam Index (FI) test measures the amount of AEA needed per gram of binder so that the foam remains stable. FI is performed by adding drops of AEA-solution, shaking and observing foam stability. It is useful for assessing the AEA dosage needed for different binder compositions. Furthermore it has given good correlation to air entrainment in concrete within three studies, even though the mechanisms of foaming and concrete air entrainment are quite different.

Combining FI-tests and adsorption studies with TGA and NMR showed high FI for AEA that adsorbs (SR – Saponified Rosin), both on high-carbon FA (FI very high = 193 mL/g) and on low-carbon FA (FI quite high = 18.4 mL/g). Furthermore, the FI was low for AEA that does not adsorb (FI = 4.8 for SOS – Synthetic Olefin Sulfonate) on low carbon FA. FI was high for AEAs that do not adsorb (FI = 40 and 32 for SOS and NVR - Neutralized Vinsol Resin) on high-carbon FA.

The FI and the foam stability were affected by the time dependency of the adsorption, since for the AEA that adsorbed (SR) a short test-time procedure with large AEA addition always reduced the FI compared to the slower standard dropwise addition of AEA. Furthermore, a long test time always increased FI compared to the short test procedure; that is, AEA must be added to retrieve the foam lost after 1 h waiting. FI is practically unaffected by time for the AEA that does not adsorb (SOS), as the foam remains stable after 1h.

The relation between adsorption and foaming and the expected relation to concrete air entrainment, as well as the changes of the AEA caused by adsorption that were observed by NMR, warrant more studies in search of robust air entrainment for fly ash concrete.

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# The effect of by-products on frost-salt durability of aged concrete

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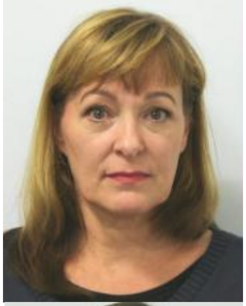

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## ABSTRACT

The evaluation of concrete performance is traditionally based the analysis of a single deterioration mechanism. However, in real life environmental conditions, concrete structures are subject to simultaneous action of several deterioration mechanisms. These can have a synergetic or cancelling effect on the degradation rate of concrete. The natural ageing of concrete exposed to the environmental is a complex phenomenon influenced by cement hydration, drying, carbonation, etc. Research on the effects of ageing on concrete durability performance has shown it to be either positive or negative, depending on concrete composition,

binder type, testing procedures, etc.
Reliable considerations of the effects of ageing on concrete performance service life are important for realistically assessing the service life of concrete structures. In Finland there is work underway to determine how different cements and binder materials should be evaluated with regards to ageing and frost-salt scaling resistance. This paper presents the results of the effect of five different ageing conditions on the frost-salt scaling performance of concrete using natural and accelerated ageing methods. Concrete specimens were subject to one or two rounds of combined ageing – degradation mechanisms. The results show that the ageing procedure influences the frost salt scaling performance of the concrete which is not considered in the standardized test setup. Concrete subject to carbonation typically shows increased scaling.
Blast furnace slag seems to improve performance in tested concretes after ageing, maybe due to good quality air entrainment, while early age frost-salt scaling performance testing is not favorable due to the effects of delayed hydration. The performance of concretes with fly ash was inferior to that of blast furnace slag, but a lower quality air void system could also be an influential factor in the test cases.

**Key words:** Durability, frost salt-scaling, carbonation, slag, fly ash, testing, ageing, drying.

## 1. INTRODUCTION

### 1.1 Coupled deterioration and ageing

Concrete performance is traditionally assessed based on deterioration caused by a single mechanism. Yet in field exposure, concrete is affected by simultaneous environmental and conditional exposures, possibly with a synergetic effect on the degradation rate of concrete. There are several interacting deterioration processes that are known but not comprehensively understood. For instance, frost deterioration may affect chloride penetration and carbonation because of the possible cracks generated by frost action.

The ageing of concrete is influenced by several factors including hydration, surface carbonation, drying and changes of the cement paste microstructure. Ageing considerably changes the cement paste pore structure, and thus also moisture behaviour. This influences the capillary water uptake, water uptake during freezing, and also freezable water content, therefore also impact concrete durability properties and thus the service life of the concrete [1-3].

The effects of concrete ageing on microstructure and durability have been studied already for decades [2-4]. Utgenannt & Petersson [5] showed that for concrete specimens of identical age, the salt-frost resistance was significantly different when exposed to different preconditioning climates before being subject to the freeze/thaw test. It was shown that the superficial surface layer of concrete determining the scaling resistance is thin and that the properties determining the scaling resistance might be affected by carbonation [5]. Uncertainty still remains on how ageing at normal climatic conditions will affect concrete frost-salt scaling. One reason for this is that with different cements, additions, additives and also with different air contents, there can be decisive impacts on the results.

The benefits of using blast furnace slag and fly ash as partial cement replacement with regards to mechanical and durability performance of concrete is well documented [6-11]. However, researchers have documented the poorer frost-salt scaling performance of these concretes in laboratory tests [12-15]. It has been indicated that the frost-salt scaling performance decreases with the addition of fly ash, which could be partially related to their delayed hydration [16-20]. Also for concrete with slag additions, a reduction in the frost-salt scaling performance was reported [5, 21-22]. These concretes are more susceptible to drying out and reduced hydration during the early stages of curing, than normal Portland cement concretes. The surface concrete is subject to greater carbonation due to the concrete’s lower alkalinity as a result of its lower calcium hydroxide (CH) content, when compared to ordinary Portland cement concrete [23, 24]. Hence the importance of longer curing for concretes containing high levels of slag. Carbonation makes blast furnace slag concrete more vulnerable to scaling under the combined load of frost attack and de-icing salts [25-29].

Overall, the detected effects of ageing have been either positive or negative, depending on the concrete composition, as well as on the testing procedures, ageing time and circumstances.

## 1.2 Overview of the DuraInt Research Project

The results presented in this paper derive from the Finnish DuraInt project (Effect of Interacted Deterioration Parameters on Service Life of Concrete Structures in Cold Environments, 2008 – 2011). The DuraInt project was funded by TEKES (Finnish Funding Agency for Technology and Innovation) together with the Finnish Transport Agency (FTA) and industry partners. The research was developed in conjunction with Aalto University as well as industry partners involved in concrete production. The research included testing over 40 mixtures in the laboratory and in in-situ exposure conditions at two Finnish field stations. The studies took into account simultaneous frost or salt-frost deterioration, chloride penetration and carbonation of different concretes. The projects also considered alternative binder materials, concrete mix designs and changing environmental conditions.

To study the interaction between different deterioration actions an extensive laboratory program was undertaken. The laboratory tests were closely linked to tasks of long term field testing [30], laboratory testing [31], deterioration modelling and service life design [32, 33].

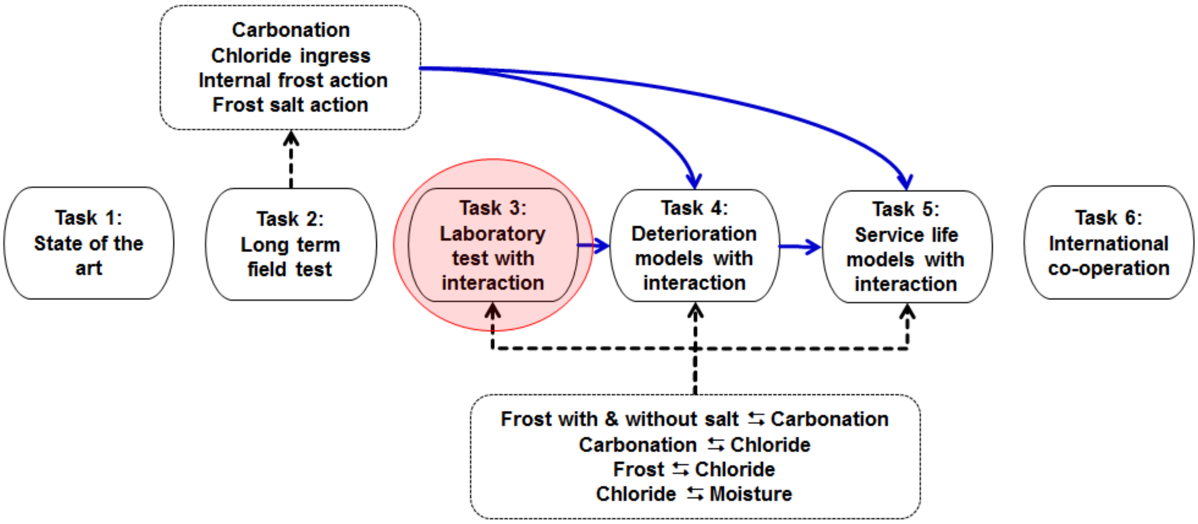

*Figure 1 – DuraInt project research work plan with identification of task where results presented in this paper derive from.*

In Figure 1 a schematic overview of the DuraInt Project work plan is presented. The results presented in the paper concern Task 3: Laboratory testing with interaction, which provided the basis for both Task 4: Modelling degradation interaction and Task 5: Modelling service-life. The reports of all the tasks can be downloaded from the internet at www.vtt.fi/sites/duraint.

## 2. MATERIALS AND CONCRETE MIXES

### 2.1 Materials

The concretes used in this research were produced with common Finnish cements and additions (blast furnace slag and fly ash). The chemical and physical characteristics of the cements and additions can be found in the Annex (Table A.1). Granitic aggregates were used with a maximum aggregate size of 16 mm. Two distinct superplasticizers were used in the concrete mixes: polycarboxylate (VB-Parmix) and polycarboxylate ether (Glenium 51). In addition, a fatty acid soap air entraining agent (Ilma-Parmix) was also used in all but one mix. Detailed information regarding the used materials can be found in the DuraInt project reports [30, 31].

### 2.2 Concrete mix design

The concrete mixes represented prevailing common industrial mixes in Finland, and mainly air entrained bridge concretes. The binder content varied between 387 and 450 kg/m$^3$. Most mixes were produced with an effective water/binder ratio (water/(cement+2·SF+0.8·BFS+0.4·FA)) of ≈ 0.42. Concrete mixing and specimen casting was done at VTT laboratory or at Rudus Oy ready mixed concrete plant.

The main mix design information, i.e. binder materials, aggregates, w/b and fresh concrete air content (measured value) and workability, is presented in the Annex (Table A.2). Standardized cubes (150×150×150 mm$^3$) were cast for laboratory testing. The specimens where handled and cured following standardized or well-defined procedures until the time of conditioning for the various testing procedures.

## 3. WORKPLAN AND TESTING

The aim of this research was to understand the effect of additions on the freeze-thaw resistance with de-icing salt when subject to varying surface ageing conditions. The effect of five different ageing conditions (exposure cases - EC) on the frost-salt scaling performance of concrete is analysed, using natural or accelerated ageing methods. Exposure cases A – C were subject to one round of combined ageing – degradation mechanisms, and exposure cases D and E were subject to an additional round of combined ageing – degradation mechanisms (see Figure 2).

### 3.1 Exposure/Ageing conditions

The five different ageing conditions are described as:

- *Exposure Case - A.* Concrete specimens were subject to the standardized frost-salt resistance test of 56 cycles with measures of the amount of scaling (kg/m$^2$).
- *Exposure Case - B.* Concrete specimens were stored at 65 % relative humidity (RH) and 20°C for a period of approximately 1.2 – 1.3 years. The specimens were considered to be aged and carbonated. The average concentration of $CO_2$ in the laboratory environment was approximately 0.00075 kg/m$^3$. At this age, the concrete specimens were subject to the same frost-salt resistance test as in EC-A.
- *Exposure Case - C.* Concrete specimens were stored for approximately 1.6 years in the same conditions as in EC-B. A 10 mm layer was sawed off the surface to remove the carbonated concrete. The concrete specimens were considered to be aged, but not carbonated. It was assumed that the new testing surface has a same drying degree than the specimens in EC-B. The concrete specimens were subject to the same frost-salt resistance test as in EC-A. Prior to testing, specimens were re-saturated as soon as possible after the sawing and rubber sheet gluing. Re-saturation was performed at the same time for all the specimens. For practical reasons, this meant that specimens had to wait for the re-saturation (<2 days) at 65 % relative humidity (RH) and 20 °C, which may have resulted in minor surface carbonation.
- *Exposure Case - D.* The concrete specimens which were tested aged but without carbonation (EC-C) were re-tested after an additional ageing period of 56 days at 1 % $CO_2$ (accelerated carbonation) followed by 11 month storage wrapped in plastic at 65 % RH and 20 °C. Then the specimens were re-tested according to the same frost-salt resistance test as in EC-A.
- *Exposure Case - E.* The concrete specimens which were tested aged and with carbonation (EC-B) were retested after an additional ageing procedure, identical to that described in EC- D.

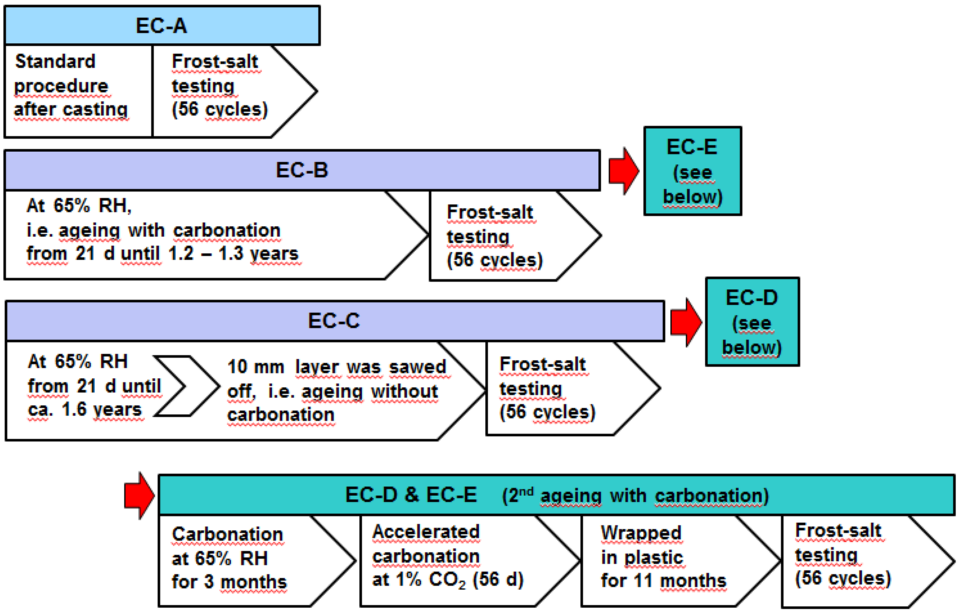

*Figure 2 – Research work plan.*

## 3.2 Testing procedures

In the following a brief description of the testing procedures used are given:

- *Compressive strength* – determined at 28 days according to SFS EN 12390-3 [34]. Each result represents the average of three 150 mm cubes.
- *Fresh air and workability* – determined according to SFS-EN 12350-7 [35] and SFS-EN 12350-2 [36], respectively.
- *Air void parameters of hardened concrete* – determined by thin section analysis according to a Finnish testing method, also used in the quality control of frost resistant concrete in Finland. The analysis is similar to ASTM C 457 [37], but performed according to the Finnish point-count method VTT TEST R003-00 [38] (SFS 7022 [39]). Usually the analysis is made by using epoxy impregnated thin sections. Only pores d = 0.02 – 0.80 mm (d = traverse length in thin section analysis plane) are included in the calculation of the specific surface area and spacing factor. This means that compaction pores are not included. In addition, the amount of pores < 0.300 mm was analysed.
- *Frost-salt scaling resistance* – tested according to CEN/TS 12390-9 [40]. The adopted testing method was the slab test with 3 % NaCl solution. In addition to surface scaling, the internal deterioration was also measured by ultrasound as the relative dynamic modulus of elasticity (RDM) according to CEN/TR 15177 [41]. The total number of cycles was 56 per round of exposure.
- *Resistance to carbonation* – the accelerated carbonation test was performed according to the standard SFS EN 13295 [42], with a concentration of 1 % $CO_2$, for 56 days. The carbonation depth was measured according to the procedure described in SFS-EN 14630 [43] by applying phenolphthalein indicator on a freshly broken concrete specimen.

Figure 3 illustrates the difference in testing in between Exposure Cases B and C. More detailed information on the fresh and hardened concrete testing methods is included in DuraInt project reports [30, 31].

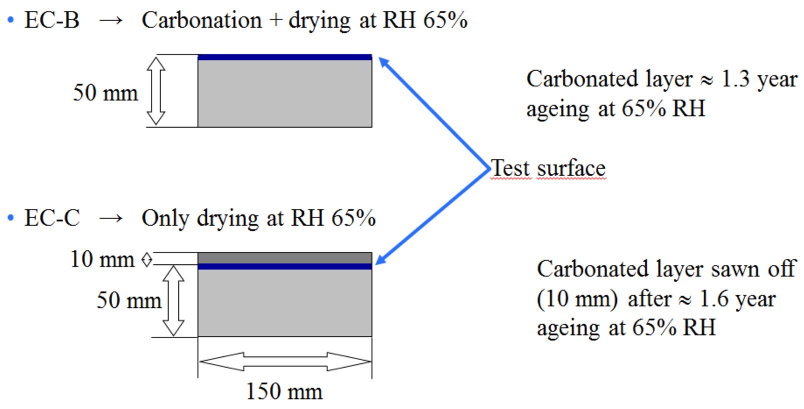

*Figure 3 – Difference between testing specimens for Exposure Cases B and C.*

# 4. RESULTS AND DISCUSSION

## 4.1 Basic properties

The average compressive strength results and the main results of the air void parameters of the hardened concrete mixes, namely, the spacing factor (mm), the specific surface area (mm$^2$/mm$^3$) and the content of pores < 0.300 mm (%), are presented in Table 1. The 28 day compressive strength of the mixtures varied between 38.0 – 58.5 MPa. The content of pores < 0.300 mm varied between 0.6 – 3.5%; the specific surface area (pores < 0.800 mm) varied between 16–37 mm$^2$/mm$^3$; and the spacing factor varied between 0.18–0.35 mm. These results reflect the very different air pore structures present in the different mixes.

Based on the results it was expected that, prior to testing frost-salt resistance, certain mixes would not perform adequately due to the poorer air pores structure. This is the case for mixes M4 and M6 where the percentage of pores smaller than 0.3 mm is very small. The maximum allowable requirement in Finland for general bridge concrete frost scaling is 0.50 kg/m$^2$, and in more demanding exposure or service life cases the maximum value is 0.20 kg/m$^2$ [40, 44].

*Table 1. Testing results: compressive strength, hardened concrete air void parameters.*

| Mix Ref. | Compressive strength (28 d) [MPa] | Pores <0.300 [%] | Specific surface area [mm$^2$/mm$^3$] | Spacing factor (pores <0.8 mm) [mm] |
|---|---|---|---|---|
| M1 | 46.4 | 3.5 | 16 | 0.35 |
| M2 | 38.0 | 2.8 | 21 | 0.28 |
| M3 | 41.2 | 2.2 | 28 | 0.24 |
| M4 | 58.5 | 0.6 | 34 | 0.33 |
| M5 | 46.0 | 2.6 | 37 | 0.18 |
| M6 | 54.6 | 1.6 | 27 | 0.30 |

## 4.2 Frost salt scaling for Exposure Cases A - C

In Table 2 the frost-salt scaling results for 28 and 56 cycles are presented for Exposure Cases A, B and C. In Figures 4 and 5 the results are presented in conjunction with the depth of carbonation for Exposure Case C.

*Table 2. Testing results: frost-salt scaling (kg/m$^2$) results for Exposure cases A, B and C.*

| Mix Ref. | EC-A | | EC-B | | EC-C | |
|---|---|---|---|---|---|---|
| | 28 cy. | 56 cy. | 28 cy. | 56 cy. | 28 cy. | 56 cy. |
| M1 | 0.04 | 0.05 | 0.47 | 0.53 | 0.08 | 0.09 |
| M2 | 0.19 | 0.20 | 0.30 | 0.42 | 0.08 | 0.09 |
| M3 | 0.18 | 0.21 | 0.45 | 0.73 | 0.22 | 0.27 |
| M4 | 0.06 | 0.08 | 1.22 | 1.55 | 0.54 | 0.98 |
| M5 | 0.20 | 0.32 | 0.39 | 0.44 | 0.02 | 0.04 |
| M6 | 0.09 | 0.16 | 0.75 | 0.80 | 0.07 | 0.09 |

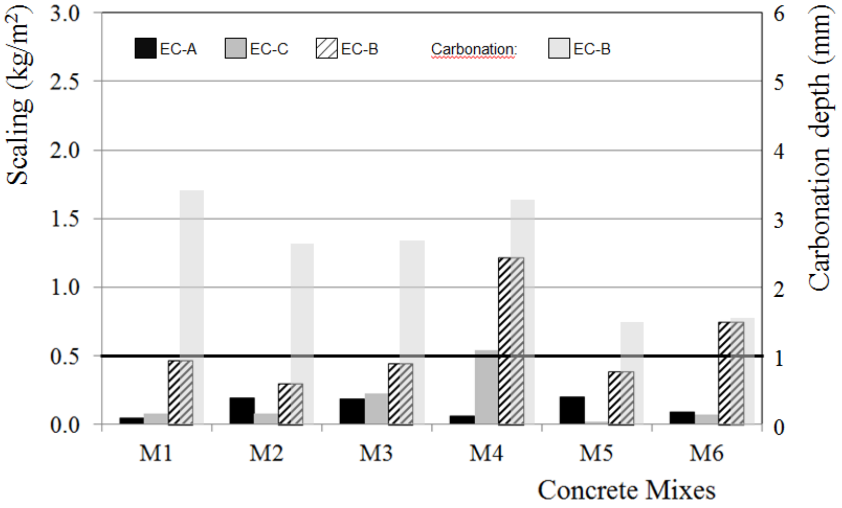

*Figure 4 – Frost-salt scaling results for Exposure cases A, B and C after 28 cycles and carbonation depths for Exposure case B.*

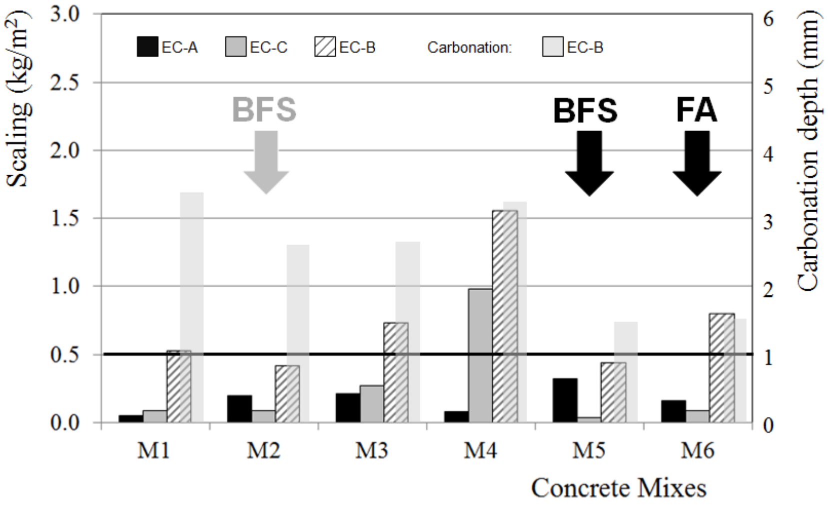

*Figure 5 – Frost-salt scaling results for Exposure cases A, B and C after 56 cycles and carbonation depths for Exposure case B.*

All concretes tested to 56 cycles, with reference exposure conditions according to the test standard, performed adequately when compared to the performance requirement of 0.5 kg/m$^2$. For the concretes that were aged, but not carbonated (EC-C), all performed adequately except mix M4 which had doubled the required allowable limit. In addition, concretes with fly ash or blast furnace slag performed better than the same concrete having the reference curing and testing.

When the same concretes where aged and carbonated, it is apparent that the amount of scaling increases in all concretes. Only the concretes that contained blast furnace slag fulfilled the performance requirement after 56 cycles. In the case of concrete mixes M4 and M6, the poorer results are partially influenced by the lower quality of their air entrainment. However, with the exception of mix M4, the other mixes that did not fulfil the requirement were by a small margin. The depth of carbonation was in general greater that the depth of scaling. In addition, the carbonation depth was lower in mixes M5 and M6 which had higher contents if blast furnace slag and fly ash, respectively, than the other mixes.

The initially faster scaling of concrete containing slag may be explained, among other factors, by the carbonation of the weak and porous surface layer of concrete, the delayed hydration of the slag which may form a weak layer with a higher water/binder ratio close to the surface, and secondly, not enough curing time due to a lower hydration of blast furnace slag concrete. It has been suggested that this is due to the recrystallisation of calcium carbonate in the surface layer [46]. The surface layer of slag containing concrete can include (besides calcite) also metastable calcium carbonates which are soluble in NaCl. It was found that, after the action of de-icing agents, only weakly crystallised calcite existed [45].

## 4.3 Frost salt scaling for Exposure Cases D and E

In Table 3 the frost-salt scaling results after 56 cycles for Exposure Cases D and E as well as the average depth of carbonation are presented. In Figures 6 and 7 the results are presented in conjunction with the depth of carbonation for Exposure Case C.

*Table 3. Frost-salt scaling results (for EC-D and EC-E).*

| Mix. Ref. | Exposure Case D | | Exposure Case E | |
|---|---|---|---|---|
| | $X_{carb}$ (mm) | scaling 56 cy.(kg/m$^2$) | $X_{carb}$ (mm) | scaling 56 cy.(kg/m$^2$) |
| M1 | 1.9 | 0.70 | - | - |
| M2 | 2.2 | 0.37 | 3.4 | 0.10 |
| M3 | 1.8 | 0.88 | 2.6 | 0.07 |
| M5 | 1.5 | 0.22 | 1.9 | 0.04 |
| M6 | 1.7 | 0.89 | 1.4 | 0.06 |

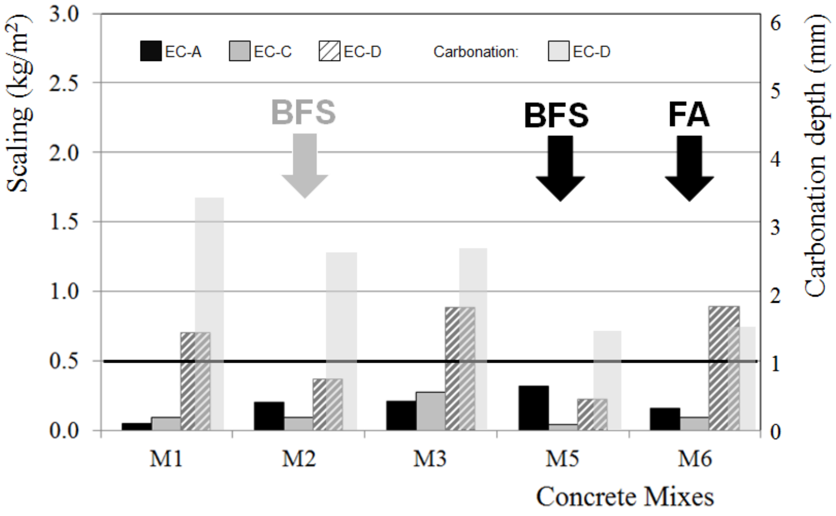

*Figure 6 – Frost-salt scaling results for Exposure cases A, B and D after 56 cycles and the carbonation depths for Exposure case D.*

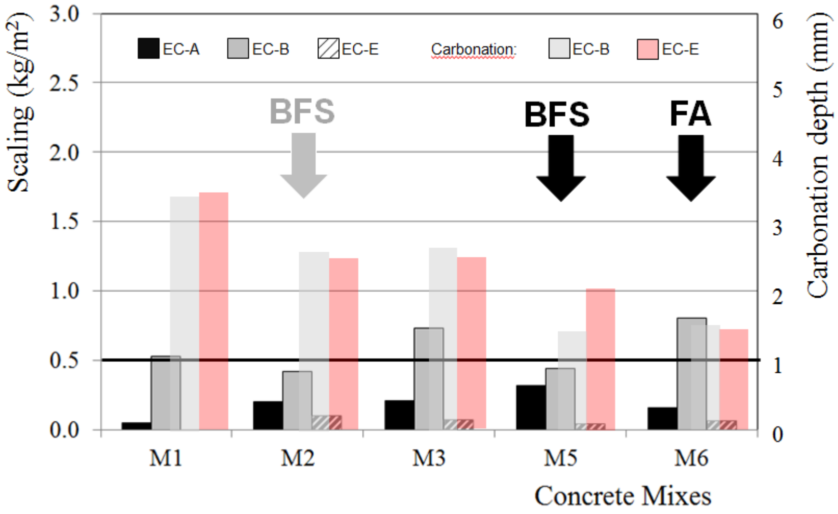

*Figure 7 – Frost-salt scaling results for Exposure cases A, C and E after 56 cycles and the carbonation depths for Exposure cases C and E.*

The results presented in Figure 6 confirmed that which was previously observed in Exposure Case C – where the carbonation had a significant influence on the increase of scaling. In this case, the concrete was aged without carbonation in the first round of testing and performed even better than the reference tests. However, when carbonated in the second round, again all the concretes performed worse than the reference testing. All concretes except those with slag exceeded the reference scaling requirement.

In Figure 7 the results of the second exposure round when the concrete was subject to a second carbonation action are presented. The depth of carbonation in the second round is measured in relation to the apparent surface at the time of testing. After the second carbonation round, all concretes show almost no additional scaling of concrete. The type of carbonation exposure that the concrete is subject to can be an influencing factor. In the first exposure round, the concrete was subject to natural carbonation for more than a year, and in the second, in addition to a 3 month period of natural carbonation, the concrete was also subject to accelerated carbonation.

No accelerates scaling was observed of the concrete specimens. Maybe due to the already carbonated surface the additional exposure to $CO_2$ did not have a significant effect. In natural carbonation conditions, the concrete surface could be subject to micro cracking, possibly due to carbonation induced shrinkage and/or drying. When the concrete is subject to accelerated carbonation conditions, only the immediate chemical reaction is measured but no long term effects are felt.

## 5. CONCLUSIONS

The research presented in this paper was based on a limited number of variables and the testing was only based mainly on unconventional test methods, which might not reflect the performance of concrete when subject to ageing. However, based on the test results obtained, the following conclusions are considered:

i. The frost-salt resistance of concretes with different binding materials is influenced by the effect of ageing.
ii. The effect of ageing in the reference test setup is not considered.
iii. All concretes subject to natural carbonation, including long term drying at 65% relative humidity, prior to testing showed worse frost-salt performance;
iv. The effect of ageing on frost-salt resistance is also different for concretes with different air pore contents and structures (distribution, content of small pores) – only concrete with similar quality of air void structure should be compared;
v. The use of blast furnace slag seems to improve performance in tested concretes after ageing – the reason could possibly be related to the good air entrainment. Early age frost salt performance testing was not favourable to concrete with this addition due to the effects of delayed hydration;
vi. The performance of fly ash was inferior to BFS, but concrete with lower quality air void system could be an influential factor in this case.

## ACKNOWLEDGEMENTS

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*Table A1 – Chemical composition and physical characteristics of binders and additions*

| Binder | | Chemical composition [%] * | | | | | | | | | Physical characteristics | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Type | Name | CaO | SiO2 | Al2O3 | Fe2O3 | MgO | SO3 | Na2O/ K2O | Free lime | C3A | γS [kg/m3] | LOI [%] | Blaine [m2/kg] | Slag [%] | Flyash [%] | Limestone [%] |
| CEM I 42,5 N - SR | Finnsementti SR-sementti (Lappeenranta) | 63 | 21 | 3,3 | 4,0 | 2,9 | 3,1 | 0,52/ 0,43 | 2,5 | 2,0 | 3,01 | 2,2 | 330 | 0 | 0 | 1 |
| CEM II/A-M (S-LL) 42,5 N | Finnsementti Yleissementti (Parainen) | 65 | 21 | 5,2 | 3,1 | 2,6 | 3,1 | 0,31/ 1,2 | 1,8 | 8,5 | 3,12 | - | 380 | 7 | 0 | 6 |
| CEM II/A-LL 42,5 R | Finnsementti Rapidsementti (Parainen) | 65 | 21 | 5,2 | 3,1 | 2,6 | 3,7 | 0,56/ 1,2 | 1,8 | 8,5 | 3,15 | - | 440 | 1 | 0 | 6 |
| CEM I 52,5 R | Finnsementti Pikasementti (Lappeenranta) | 64 | 21 | 4,3 | 3,0 | 2,9 | 3,5 | 0,6/ 0,53 | 2,0 | 6,5 | 3,10 | 1,7 | 530 | 0 | 0 | 2 |
| Blast furnace slag – KJ400 | Finnsementti Masuunikuona-jauhe | 40 | 34 | 9,3 | - | 11 | - | 0,47/ 0,47 | - | - | 2,97 | - | 400 | 100 | 0 | 0 |
| Flyash | - | 4-7 | 45-55 | 20-30 | - | 3-5 | - | 1-2 | - | - | 2.20 | - | ≈ 250 | 0 | 100 | 0 |

**For cements – based on average clinker composition from June - December 2007*

*Table A2 – Concrete mix design, fresh air content and workability.*

| REF | CEM type | Cement content [kg/$m^3$] | Addition content [kg/$m^3$] † | w/b ratio * [-] | Water [l/$m^3$] | Aggregates | | | | Plastisizer | | Air-entraining agent | | Fresh air [%] | Slump [mm] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Total [kg/m3] | < 0,125 mm [%] | < 0,250 mm [%] | < 4 mm [%] | Product | Amount [% all binder] | Product | Amount [% all binder] | | |
| M1 | CEM I 42,5 N - SR | 387 | - | 0.42 | 161 | 1796 | 4 | 11 | 50 | G 51 | 0.78 | I-P | 0.017 | 5.9 | 115 |
| M2 | CEM II/A-M(S-LL) 42,5 N | 428 | - | 0.42 | 179 | 1709 | 3 | 9 | 49 | G 51 | 0.8 | I-P | 0.014 | 5.9 | 180 |
| M3 | CEM II/A-LL 42,5 R | 421 | - | 0.42 | 176 | 1748 | 3 | 9 | 49 | G 51 | 0.82 | I-P | 0.017 | 5.0 | 140 |
| M4 | CEM I 52,5 R | 417 | - | 0.42 | 175 | 1737 | 3 | 7 | 40 | VB-P | 0.873 | I-P | 0.060 | 5.5 | 80 |
| M5 | CEM II/A-LL 42,5 R + SLG | 217 | 217 SLG | 0.42 | 163 | 1725 | 2 | 7 | 36 | VB-P | 1.26 | I-P | 0.030 | 6.1 | 150 |
| M6 | CEM II/A-LL 42,5 R + FA | 344 | 106 FA | 0.45 | 173 | 1706 | 3 | 8 | 48 | G 51 | 1.01 | I-P | 0.018 | 5.0 | 170 |

*† FA – fly ash; BFS – blast furnace slag; ** Slump-flow (mm)/t500 (s); * Weff/(Cement+2*SF+0,8*BFS+0,4*FA);*
*I-P – Ilma-Parmix; G51 – Glenium G 51; VB – VB-Parmix*

# Properties of concretes mixed with pulverized fly ash and ground granulated blast furnace slag

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## ABSTRACT

In this paper investigations made at the Central laboratory of Thomas Concrete Group where the properties of concretes mixed with combinations of pulverized fly ash or ground granulated blast furnace slag and Portland cement are presented. Some of the results from these investigations are presented and discussed. Generally the results show that concrete with fly ash or blast furnace slag gets properties that are equivalent to comparable Portland cement concretes. Based on these results it is concluded that the regulations in the standards EN 206-1 and SS 13 70 03 in most situations are reasonable, but in some situations too conservative.

**Key words:** Pulverized fly ash, ground granulated blast furnace slag, strength, durability, frost resistance, chloride ingress.

## 1. INTRODUCTION

### 1.1 General

There is an increasing interest of using different types of industrial by-products, e.g. Pulverized Fly Ash (PFA) from coal fired power plants or Ground Granulated Blast Furnace Slag (GGBS) from steel plants, to partly replace cement in the mixing of concrete. In this way the environmental impact, e.g. from $CO_2$, as well as the production costs are reduced compared to Portland cement (CEM I) concretes. Moreover the performance of the fresh and hardened concrete compared to CEM I concretes is in many cases also improved with additions of PFA or GGBS.

PFA or GGBS can be added to concrete either as a cement (CEM II or CEM III, where PFA and/or GGBS is inter-ground with Portland cement klinker or added to ground cement at the cement factory) or as a mineral addition at the concrete plant, where cement and PFA and/or GGBS are mixed in the concrete mixer. The latter provides larger flexibility to choose concrete composition and influence the concrete properties than if a CEM II or CEM III cement is used. At present (April 2012), however, no CEM II or CEM III cements with PFA and/or GGBS are available in Sweden. Therefore only PFA or GGBS added as an addition at the concrete plant is covered in this paper.

The properties of PFA and GGBS intended to be used as an addition in concrete is regulated in the standards EN 450-1 [1] and EN 15167-1 [2] respectively. In [1] a large number of requirements regarding the chemical and physical properties of fly ash in general are defined and it is described how these properties should be tested. However, in reality it is only fly ash from coal fired power plants, i.e. PFA, that meet these requirements. In this paper only PFA from a coal fired power plant was used. In [2] the requirements regarding chemical and physical properties for GGBS and how they should be tested are defined.

The usage of PFA and GGBS in concrete in Sweden is regulated in the standards EN 206-1 [3] and SS 13 70 03 [4]:

- **EN 206-1**. In [3] the usage of PFA and GGBS is regulated by either the concept with equivalent concrete performance concept (ECPC) or for PFA the concept with effiency factors, *k*-factors. The *k*-factors are used to describe the effects of different binders on the performance of the concrete, where usually the compressive strength is considered. With ECPC a concrete should have equivalent performance (e.g. durability) compared to a reference concrete. In this study, however, only the concept with *k*-factors has been used. In [3] and [4] the *k*-factors are normally prescribed to 0.4 for PFA and 0.6 for GGBS.
- **SS 13 70 03**. The dosages of PFA and GGBS are regulated in [4], where the maximum contents that are allowed to mix in depend on the exposure conditions, where the lowest contents are allowed in rough environments with exposure to chloride and frost, i.e. in exposure classes XS 3, XD 3 and XF 4 (described in [3]), where an addition of 25 wt-% (PFA & GGBS) of CEM I is allowed.

In Sweden, concrete for civil engineering structures (and housing structures, but these are not covered in this paper) are also regulated in AMA (General description of material and execution of work) [5], which is a series of handbooks used to make technical descriptions. Most Swedish clients, e.g. Trafikverket (the Swedish Transport Administration), refer to this document when they make technical descriptions. In [5] additional restrictions regarding the usage of PFA are introduced, see further below. Regarding the addition of GGBS [5] refers to [4]

## 1.2 Usage of PFA and GGBS in concrete

In Sweden the usage of PFA and GGBS in concrete is regulated with the concept of effiency factors, *k*-factors. In [3-4] the *k*-factor is 0.4 for PFA and 0.6 for GGBS. In some situations higher *k*-factors may be allowed, but this requires validation by extensive laboratory testing. A replacement of up to 33 wt-% (PFA) and 100 wt-% (GGBS) of CEM I is allowed if the additions are to be included in the equivalent water-cement ratio $(w/c)_{eq}$. Larger additions are considered inactive and may therefore not be included in $(w/c)_{eq}$. The maximum amount of allowed additions of PFA or GGBS depends on the exposure conditions (exposure classes in [3]:

- X 0 & XA 1. 50 % (PFA) and 230 % (GGBS).
- XC 1-XC 2. 50 % (PFA) and 150 % (GGBS).
- XC 2-XC 4, XS 1-XS 2, XD 1-XD 2, XF 1-XF 3 & XA 2. 50 % (PFA) and 50 % (GGBS).
- XS 3, XD 3 & XF 4. 25 % (PFA) and 25 % (GGBS).

In [5] the additions of PFA are, however, limited to 6 % (in XF 4) and 11 % (in other exposure classes) of the cement weight, in bridge structures. For other civil engineering structures [5] refers to [4] regarding allowed additions of PFA. Regarding additions of GGBS [5] refers to [4].

The regulations in standards regarding *k*-factors and additions of PFA or GGBS reflect the worst case, i.e. PFA or GGBS that are just meeting the requirements in the standards [1-2] is used, which means that the *k*-factors and additions are conservative (low). If PFA or GGBS with better quality is used higher values of *k*-factor and/or higher amount of allowed additions could be used. At the Central laboratory of Thomas Concrete Group investigations of the properties of PFA or GGBS in concrete have been made, to quantify the actual *k*-factors and determine if the allowed additions of PFA or GGBS in [3-4] are reasonable.

### 1.3 Properties of PFA and GGBS

PFA is a by-product from coal fired power plants, which consists of the remaining of the coal after passing the furnace. PFA consists mainly of spherical amorphous particles (60-90 wt-%), different forms of crystalline particles, and unburned coal [6]. The amorphous particles, which give PFA its puzzolanic properties, are created when the remaining of burnt coal rapidly is cooled down in the exhaust gas (and collected by electrostatic precipitators). Important factors that are influencing the properties of PFA are its glass content, the amount of unburned coal, fineness and the specific surface.

GGBS is a by-product from manufacturing of steel, which is collected from the upper part of the blast furnace. In the lower part of the blast furnace the molten iron is collected. The slag has to be cooled rapidly by immersion in water so that a glassy granulated material is formed to get appropriate properties for usage as a cementitious material. Before usage the granulated material has to be ground to a fine powder with a specific surface of approximately 400-500 $m^2/g$. Typically GGBS consists of more than 95 wt-% of silicon, calcium, aluminium magnesium and oxygen. Important factors that are influencing the properties of GGBS are its chemical composition, glass content, fineness and the specific surface. [7-8]

### 1.4 Properties of concrete mixed with PFA or GGBS

The performance of concretes mixed with PFA or GGBS is well documented in the literature for most properties. Many properties are improved when additions of PFA or GGBS are used compared with the cases if only CEM I is used, for example [6-8]:

- **General**. When PFA or GGBS is added to concrete it partly replaces CEM I, which in its turn means that the amount of CEM I can be reduced. This reduction results in less amount of energy needed in the concrete production and, as a consequence, less environmental impact. Additionally the expenditures for the concrete can also be reduced, since PFA or GGBS usually is cheaper than CEM I.

- **Fresh concrete**, where the workability is improved, when additions of PFA or GGBS are used. Normally concrete with PFA or GGBS also has less bleeding problems. However, the risk of bleeding depends on the fineness of the GGBS, where it decreases for finely ground GGBS and may increase if coarser ground GGBS is used.
- **Young concrete**, where heat development is lower whilst strength development is slower. This is beneficial in some structures, e.g. in massive cross-sections where there is risk of temperature cracking.
- **Hardened concrete**, where strength development is slower up to an age of 28 days, but larger after 28 days, compared to CEM I concrete. Furthermore the durability is improved in many aspects, e.g. in structures subjected to chloride or sulphate attacks, cf. [6-16]. However, for other types of attacks, e.g. frost attack, there are fears that the performance of concrete with PFA or GGBS is slightly worse than for CEM I concrete, especially with larger additions of PFA or GGBS.

From the list above it is obvious that concretes with PFA or GGBS get not only improved properties, but also reductions in environmental impact and energy use, compared to CEM I concretes. In many cases the properties are improved with increasing amounts of PFA or GGBS (up to what is allowed in [4]). However in some cases there are fears that the performance gets worse with additions of PFA or GGBS, e.g. in concrete subjected to frost attack. Therefore there is a need to clarify how the additions of PFA or GGBS influence the properties of concrete and if properties comparable with the ones for CEM I concrete can be achieved (with special focus on frost attack).

In the following chapters some results from three investigations of properties of concrete with PFA or GGBS, made at the central laboratory of Thomas Concrete Group, are presented. Special focus has been on concrete in exposure class XF4, i.e. frost attack with high water saturation and de-icing agents present. According to [4] in this exposure class the concrete must have $(w/c)_{eq}<0.45$, with a maximum allowed addition of PFA or GGBS of 25 wt-% of CEM I and *k*-factors equal to 0.4 (PFA) or 0.6 (GGBS). However, also larger additions of PFA (to 33 wt-% of CEM I) and GGBS (to 100 wt-% of CEM I) have been tested. Some of the results from these investigations are presented in the following chapters.

## 2. EFFICIENCY OF PFA OR GGBS

The quality and effiency of PFA or GGBS can be tested in several ways. Generally the results from the investigations show that the effiency (described with the *k*-factor) is not constant, but vary depending on several factors, for example: (i) The contents of PFA or GGBS, (ii) The properties of the PFA or GGBS, (iii) The properties of the cement, (iv) The concrete composition, e.g. *w/c*, (v) The temperature during the early phase of the hydration process, and (vi) The curing and age.

The efficiency of both PFA and GGBS has been studied in terms of activity index (AI), according to the procedure described in EN 196-1. AI is determined as the quotient between the strength of a mortar mixed with PFA or GGBS and cement and that of a mortar mixed with only cement (reference) at the same age. In [1-2] there are requirements of minimum AI at 28 days, AI>75 % for PFA and >70 % for GGBS. In the investigations presented in this paper PFA and

GGBS imported to Sweden by Thomas Cement has been used, see [17]. The PFA comes from BauMineral Werk Rostock and the GGBS comes from Holcim Werk Bremen. Some of the results of AI for PFA and GGBS mixed with different cements available on the Swedish market are presented in Figure 1 (PFA) and Figure 2 (GGBS).

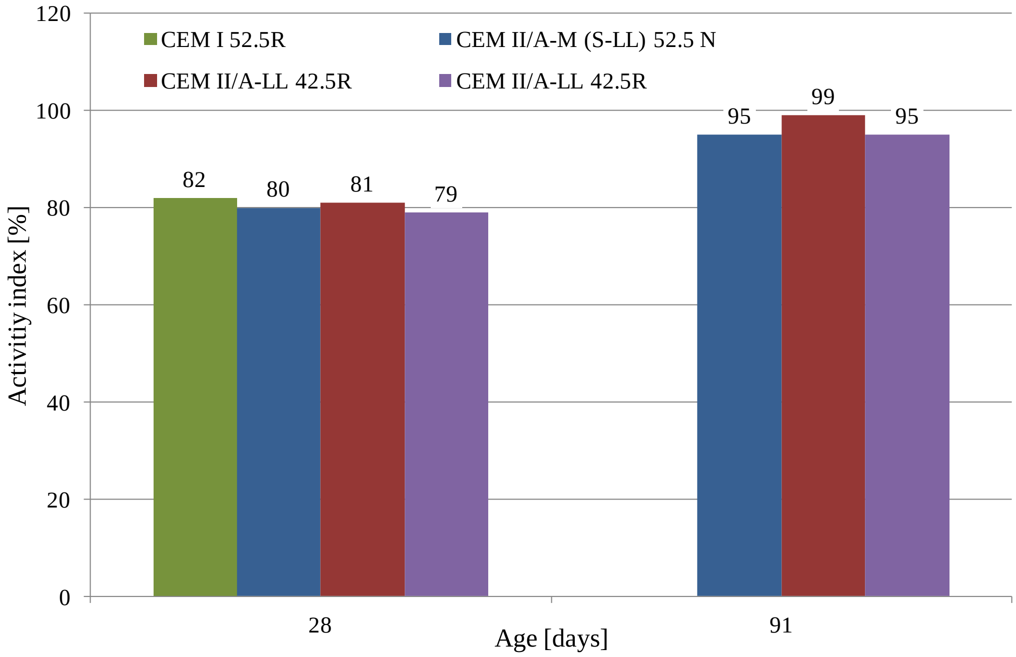

*Figure 1 – Activity index (AI) for PFA from BauMineral Werk Rostock and cements available on the Swedish market. Data from [17].*

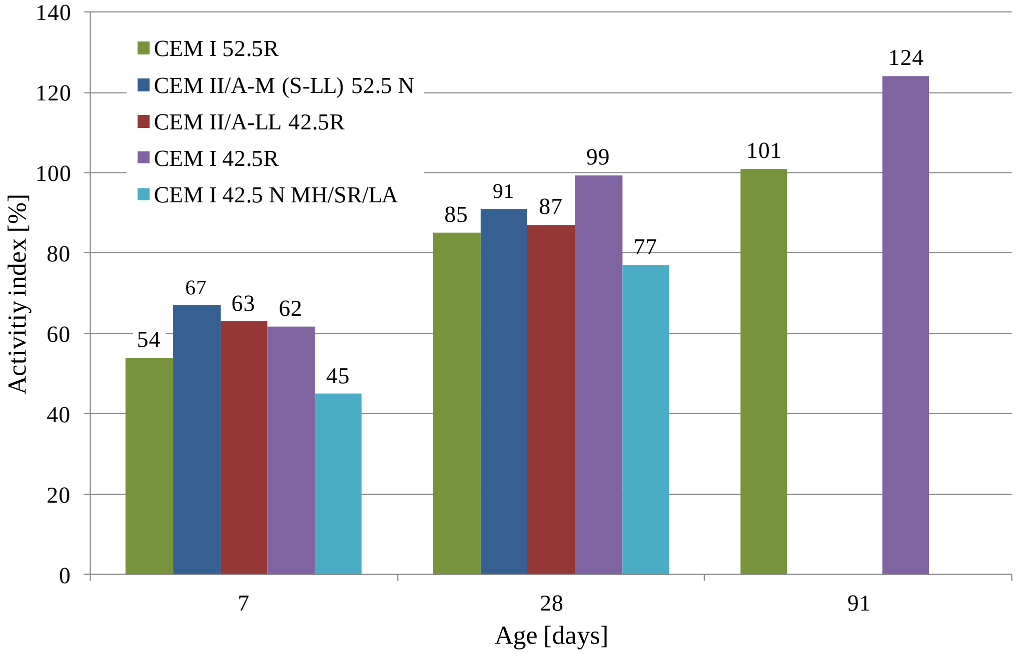

*Figure 2 – Activity index (AI) for GGBS from Holcim Werk Bremen and cements available on the Swedish market. Data from [17].*

The results in Figure 1-2 show that the AIs are significantly higher than 75 % (PFA) and 70 % (GGBS) (at 28 days). This indicates that the studied PFA and GGBS well fulfil the requirements in [1-2]. An interesting observation in Figure 2 is that there is a difference in AI depending on cement type where the highest and lowest AIs are measured for CEM I 42.5 R and CEM I 42.5 N MH/SR/LA. The latter is the most commonly used cement in civil engineering structures in Sweden, but as it is shown in Figure 1 this cement is not optimal mixed with PFA or GGBS. However, the measured AIs show that the combination CEM I 42.5 N MH/SR/LA and GGBS anyhow fulfil the requirements in [2] (AI>70 % after 28 days).

## 3. INVESTIGATIONS BY KNUTSSON (2010)

Tomas Concrete Group has in collaboration with Chalmers University of Technology participated in a Master Thesis project, where the aim was to investigate the durability of concretes with PFA, with special focus on frost durability. In the following sections a short review of the project is made. A full presentation is given in [18].

### 3.1 Concrete compositions and performed test

The concrete mixes tested by [18] fulfil the requirements specified in [4] for exposure class XF 4, i.e. $(w/c)_{eq}$=0.45. In total four different mixes were included in the investigation (with different additions of PFA and *k*-factors):

- Mix 1. 20 wt-% PFA of CEM I and *k*=0.4.
- Mix 2. 20 wt-% PFA of CEM I and *k*=1.0.
- Mix 3. No PFA (reference mix).
- Mix 4. 6 wt-% PFA of CEM I and *k*=0.4.

Cementa Anläggningscement (CEM I 42.5 N MH/SR/LA) and PFA from BauMineral Werk Rostock (Warnow Füller, which fulfils the requirements in category A in [1]) were used in all concrete mixes. The workability and air content of the concrete was adjusted by additions of superplasticizer (VR – SIKA Sikament 56/50, which is polycarboxylate based) and air entraining agent (AEA – SIKA SikaAer-S, which is a synthetic tenside). The dosages of the admixtures were regulated so the air content in the fresh concrete was kept at 4.5±0.5 %. Both the VR and the AEA were added to the mixing water. The concrete has been mixed for two minutes in a Zyklos Rotating Pan Mixer before casting. The required dosage of AEA varied between the different mixes, where the mixes with 20 % PFA required higher dosages of air entraining agent than the reference mix. Another interesting observation was that the AEA had to be combined with VR to reach the requested air content with reasonable dosages of the AEAt. This will be further discussed in chapter 6.

### 3.2 Results

Several tests have been performed on the properties of both the fresh concrete and hardened concrete. In this paper, however, only the results from testing of the compressive strength, resistance against chloride ingress and frost attack will be presented. A full presentation is given in [18].

*Compressive strength*

The compressive strength was determined on cubes (150x150x150 mm$^3$) after 7, 28, 56 or 90 days curing in water, see Figure 3. The testing was in accordance with EN 12390-3 [19].

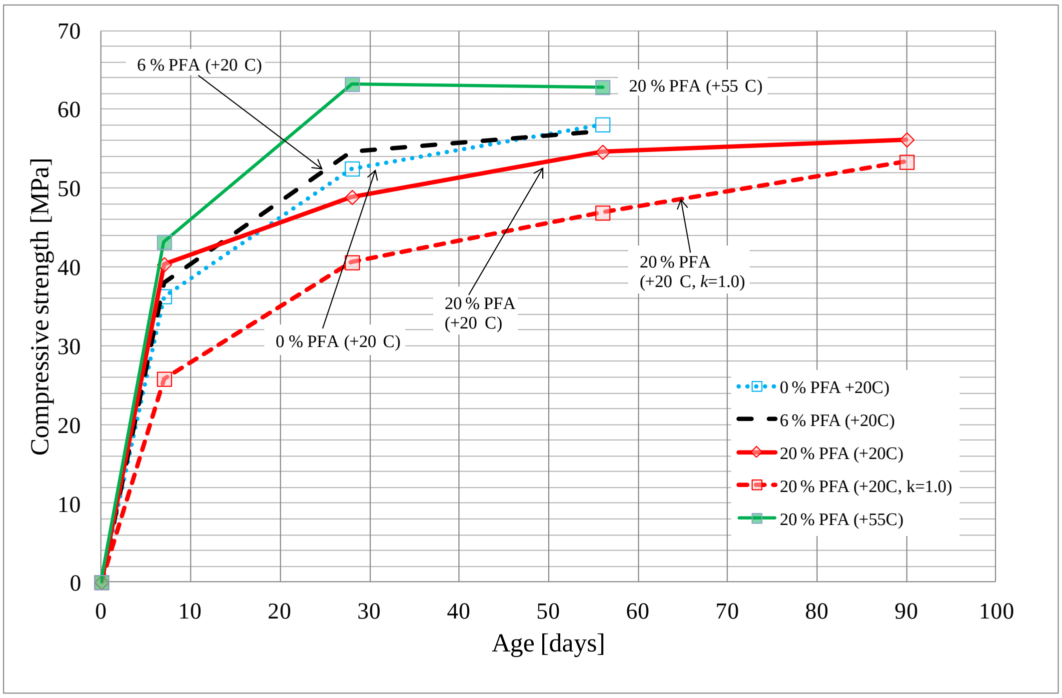

*Figure 3 – Compressive strength determined on concrete with 0-20 wt-% PFA of CEM I with different curing conditions and k-factors. Testing according to [19].*

The results in Figure 3 show that the curing conditions and the value of the *k*-factors have significant influence on the compressive strength. Curing at higher temperature has, as expected, a positive effect on the strength development where the strength after 28 days is approximately 10 MPa higher for the specimens cured in +55°C compared to the ones cured in +20°C. This is explained by the fact that the samples cured at higher temperature also have higher degree of maturity. The influence of the *k*-factor for the concrete mixes with PFA is clear, where *k*=0.4 gives almost similar strength as for the concrete mixes without PFA, while *k*=1.0 gives significantly lower strength.

*Resistance against chloride ingress - $D_{RCM}$*

The resistance against chloride ingress was determined in terms of a rapid chloride migration coefficient, $D_{\mathrm{RCM}}$, according to the method described in NT Build 492 [20]. The results from the tests are presented in Figure 4, where $D_{\mathrm{RCM}}$ for all tested concrete mixes are shown.

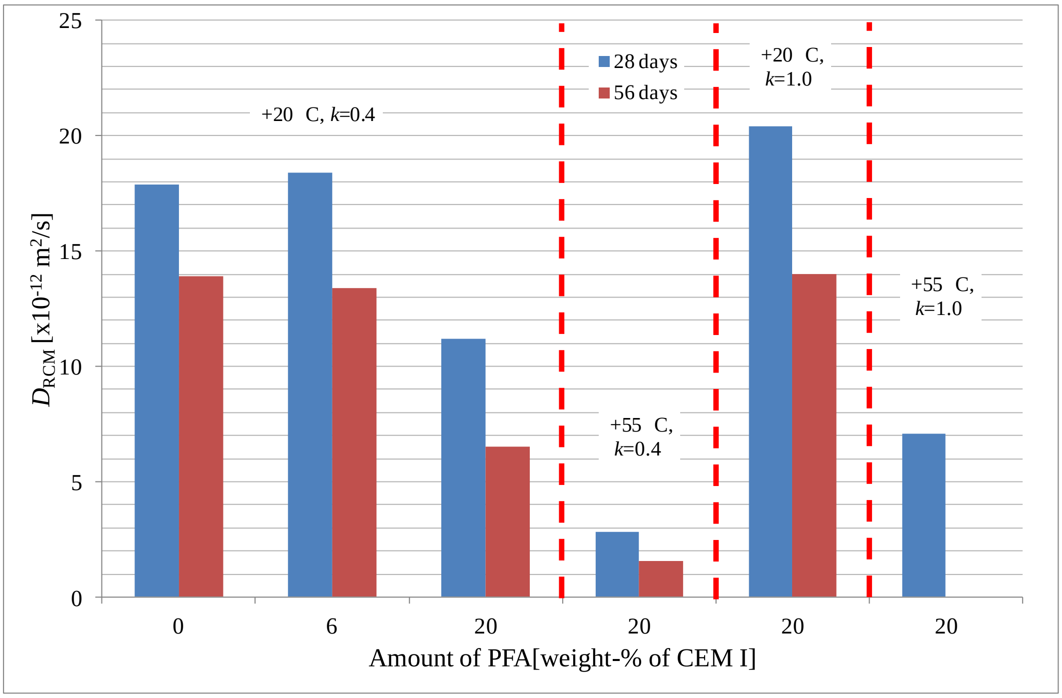

*Figure 4 – Resistance against chloride ingress determined as $D_{RCM}$ for concrete with 0-20 wt-% PFA of CEM I with different curing conditions and k-factors. Testing according to [20].*

The results presented in Figure 4 show that additions of PFA have positive effect on the resistance against chloride ingress, where $D_{RCM}$ decreases with increasing additions. Compared with the mix with only CEM I cement $D_{RCM}$ for the mix with 20 wt-% PFA of CEM I is approximately halved for 56 days curing. Prolonged curing or curing at higher temperature decreases $D_{RCM}$, also for concrete without additions of PFA. These results correspond with what is reported in the literature, where additions of up to 50 wt-% PFA (of the cement) increase the resistance against chloride ingress, see e.g. [9-12].

### *Frost resistance*

The frost resistance was determined according to the method described in the Swedish standard SS 13 72 44 [21], procedure IA (i.e. sawed surface from a cube exposed to 3.0 % NaCl-solution). In Figure 5 the results from all investigated concrete mixes are shown (with scaling measured after 28, 56 and 112 freeze/thaw cycles). The acceptance criteria for very good frost resistance (maximum accumulated amount of scaled material after 56 freeze/thaw cycles 0.10 kg/m$^2$) and good frost resistance (maximum accumulated amount of scaled material after 112 freeze/thaw cycles 0.50 kg/m$^2$) have been added to the figure. The indexes of $x$-axis indicate age of the concrete when the testing started (28-90 days) and the curing temperature (+20°C or +55°C).

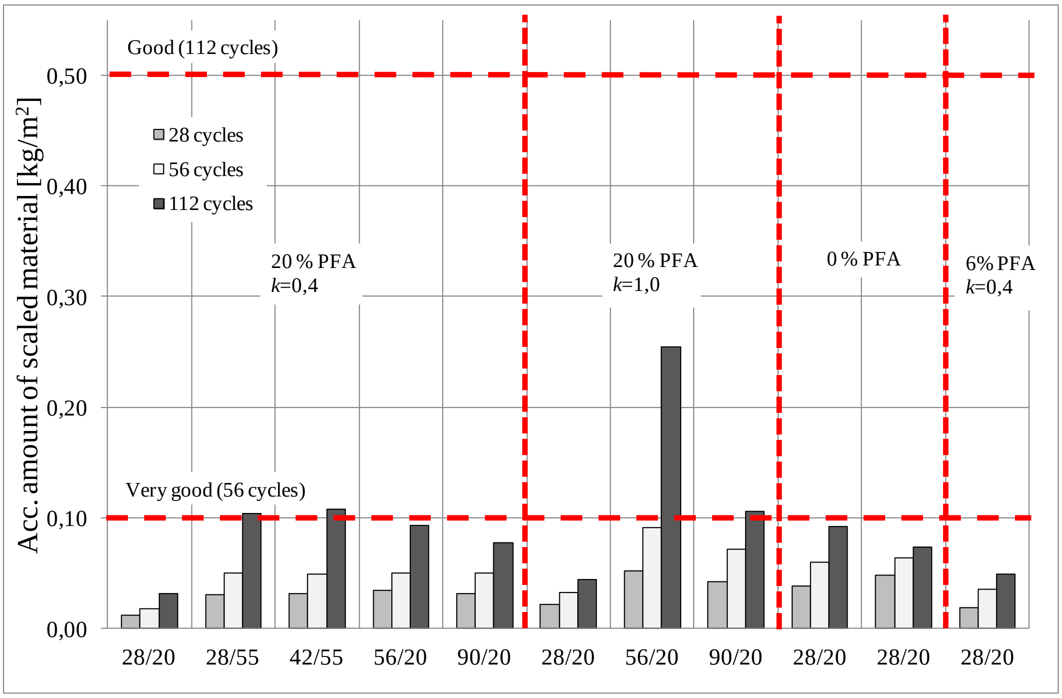

*Figure 5 – Frost resistance for concrete with 0-20 wt-% PFA of CEM I with different curing conditions and k-factors. Testing according to [21].*

The results presented in Figure 5 show that all mixes have very good frost resistance, i.e. the accumulated amount of scaled material is less than 0.10 kg/m$^2$ after 56 freeze/thaw cycles. The results show that a concrete with up to 20 wt-% PFA of CEM I has very good frost resistance as long as a good air pore system has been created. All tested concrete mixes had extra air (4.5±0.5 %) by additions of AEA.

The effect of different *k*-factors can be observed in Figure 5. When a higher *k*-factor is used it will result in a lower amount of binder, which in its turn results in a less dense pore structure and lower strength. As a result the hydraulic pressures get lower, with decreased risk of frost damage, but on the other hand the amount of freezable water increase and the strength of the concrete decreases, which worsens the frost resistance. It seems that the latter is slightly more dominant and that the frost resistance is slightly decreased when *k*=1.0, but still it is very good.

An interesting observation in Figure 5 is the effect of prolonged curing. For all concretes with PFA prolonged curing seemed to slightly increase the scaling. One possible explanation is that curing at higher temperature may result in micro cracking, which may result in larger scaling. This can, however, not explain the increased scaling after prolonged curing (i.e. 56 or 90 days before start of testing). Another explanation is therefore that the structure of the concrete gets denser after prolonged curing or curing at higher temperature, but the size of or the distance between the air pores will not be influenced. As a result the capillary pores connecting the air pores become finer and the hydraulic pressures, which occur when water is transported during freezing, may increase, resulting in a higher risk of damage of the pore structure.

## 3.3 Final comments – Knutsson (2010)

The general conclusion from the investigations by [12] is that concrete with additions of PFA (up to 20 wt-% of CEM I and that fulfils the requirements in [1]), *k*=0.4, gets properties that are equivalent to comparable CEM I concretes. If $k$=1.0 the performance is somewhat reduced compared to comparable CEM I concretes. The effects from prolonged curing or curing at higher temperatures on the properties of concrete with PFA are varying. The results from the concretes with low additions of PFA (6 wt-% of CEM I) show that there are only small differences in properties compared to CEM I concretes and thus low additions of PFA would have no noticeable effect on the concrete properties.

## 4. INVESTIGATIONS BY LINDVALL (2011)

Tomas Concrete Group has with support from the Development Fund of the Swedish Construction Industry (SBUF), made an investigation where the aim was to investigate the durability of concretes with PFA, with special focus on frost resistance. In the following sections a short review of the project is made. A full presentation is given in [22].

### 4.1 Concrete compositions and performed test

The concrete mixes tested by [22] have been proportioned so as to fulfil the requirements specified in [3] for exposure classes XD3 and XF4, i.e. $(w/c)_{eq}$=0.40 & 0.45. In total 15 different mixes were included in the investigation (with different additions of PFA, where $k$=0.4 has been used, mixed with both CEM I and CEM II cements):

- $(w/c)_{eq}$=0.40. 0-25 wt-% PFA of CEM I. Mixed with CEM I. Three mixes.
- $(w/c)_{eq}$=0.45. 0-33 wt-% PFA of CEM I. Mixed with CEM I. Six mixes.
- $(w/c)_{eq}$=0.50. 0-25 wt-% PFA of CEM I. Mixed with CEM I. Three mixes.
- $(w/c)_{eq}$=0.45. 0-25 wt-% PFA of CEM I. Mixed with CEM II. Three mixes.

The cements used have been Cementa Anläggningscement (CEM I 42.5 N MH/SR/LA) and Cementa Byggcement (CEM II/A-LL 42.5 R). The PFA used in all mixes has been BauMineral Werk Rostock (Warnow Füller, which fulfils the requirements in category A in [1]) The workability and air content of the concrete was adjusted by additions of superplasticizer (VR – SIKA Sikament 56/50, which is polycarboxylate based) and air entraining agent (AEA – SIKA SikaAer-S, which is a synthetic tenside). The dosages of the admixtures were regulated so the air content in the fresh concrete was kept at 5.5±0.5 %, slightly higher than that studied by Knutsson [18]. Both the VR and the AEA were added to the mixing water. The concrete has been mixed for two minutes in a Zyklos Rotating Pan Mixer before casting. The required dosage of air entraining agent varied between the different mixes, where the dosages of AEA had to be increased with increasing addition of PFA. Similar to [18], another interesting observation was that the AEA had to be combined with VR to reach the requested air content with reasonable dosages of the AEA. This will be further discussed in chapter 6.

### 4.2 Results

Several tests have been performed on the properties of both the fresh concrete and hardened concrete. In this paper, however, only the results from testing of the compressive strength, resistance against chloride ingress and frost attack will be presented. A full presentation is given in [22].

*Compressive strength*

The compressive strength was determined on cubes (150x150x150 mm$^3$) after 7, 28 or 56 curing in water (+20°C). The testing was in accordance with [13]. The results from the mixes with CEM I, $(w/c)_{eq}=0.45$ and with up to 33 wt-% PFA of CEM I are presented in Figure 6.

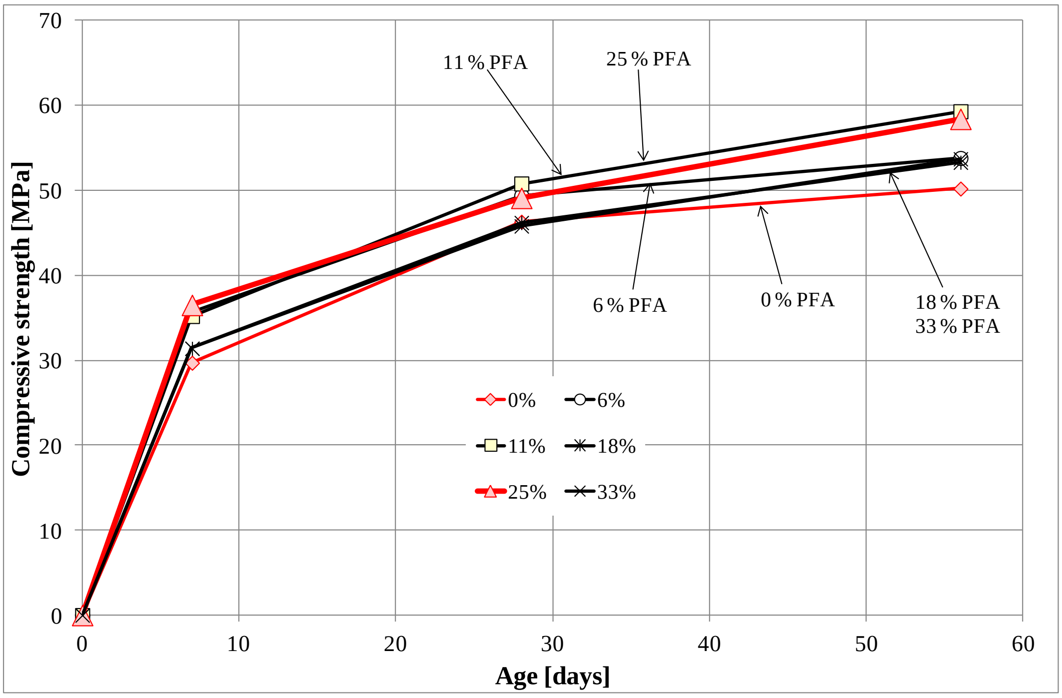

*Figure 6 – Compressive strength determined on concrete with 0-33 % PFA of CEM I at different ages (7, 28, and 56 days). $(w/c)_{eq}=0.45$. Testing according to [19].*

The effect from the curing time can be observed in Figure 6, where the strength increases with increasing curing time for all mixes. The increase of strength is more pronounced for the mixes with more than 11 wt-% PFA of CEM I, where the strength continues to increase also between 28 days and 56 days. This is mainly a result of the fact that the puzzolanic reactions of the PFA are slower than the reactions of CEM I. The differences in strength between the different mixes at 28 days (4.6 MPa) cannot solely be explained by the influence from PFA. Other factors that may influence are variations in air content and/or moisture in the aggregates between the mixes.

*Resistance against chloride ingress - $D_{RCM}$*

The resistance against chloride ingress was determined in terms of a rapid chloride migration coefficient, $D_{\mathrm{RCM}}$, according to the method described in [20]. The results from the mixes with CEM I, $(w/c)_{eq}=0.45$ and with up to 33 wt-% PFA of CEM I are presented in Figure 7.

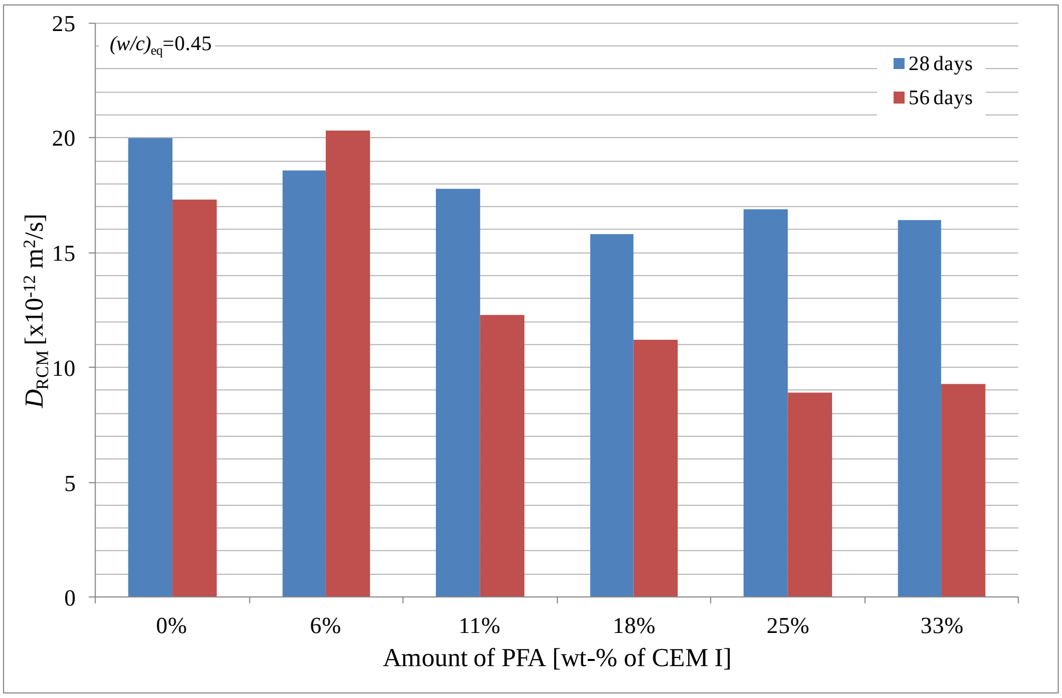

*Figure 7 – Resistance against chloride ingress determined as* $D_{RCM}$ *for concrete with 0-33 % PFA of CEM I with different curing times.* $(w/c)_{eq}=0.45$*. Testing according to [20].*

In Figure 7 it is clear that additions of PFA and prolonged curing decrease $D_{\mathrm{RCM}}$. The positive effect of prolonged curing is especially clear for the mixes with large additions of PFA (25 and 33 wt-% of CEM I). Compared with the mix with only CEM I cement $D_{\mathrm{RCM}}$ for the mix with 25 % and 33 % PFA is approximately halved for 56 days curing. This is mainly a result of the puzzolanic reactions of the PFA, which proceed slower than the reactions of CEM I. A somewhat strange result is that $D_{\mathrm{RCM}}$ for the mix with 6 % PFA of CEM I increases between 28 days and 56 days; the reason for this is not known.

*Frost resistance*

The frost resistance was determined according to the method described in [21], procedure IA (i.e. sawed surface from a cube exposed to 3.0 % NaCl-solution). In Figures 8 and 9 the results from all investigated concrete mixes are shown (with scaling measured after 28, 56 and 112 freeze/thaw cycles) after curing for 28 days, respectively. The acceptance criteria for very good frost resistance (maximum accumulated amount of scaled material after 56 freeze/thaw cycles 0.10 kg/m$^2$) and good frost resistance (maximum accumulated amount of scaled material after 112 freeze/thaw cycles 0.50 kg/m$^2$) have been added to the figure. The indexes of *x*-axis indicate $(w/c)_{\mathrm{eq}}$ and the amount of PFA added to the mix.

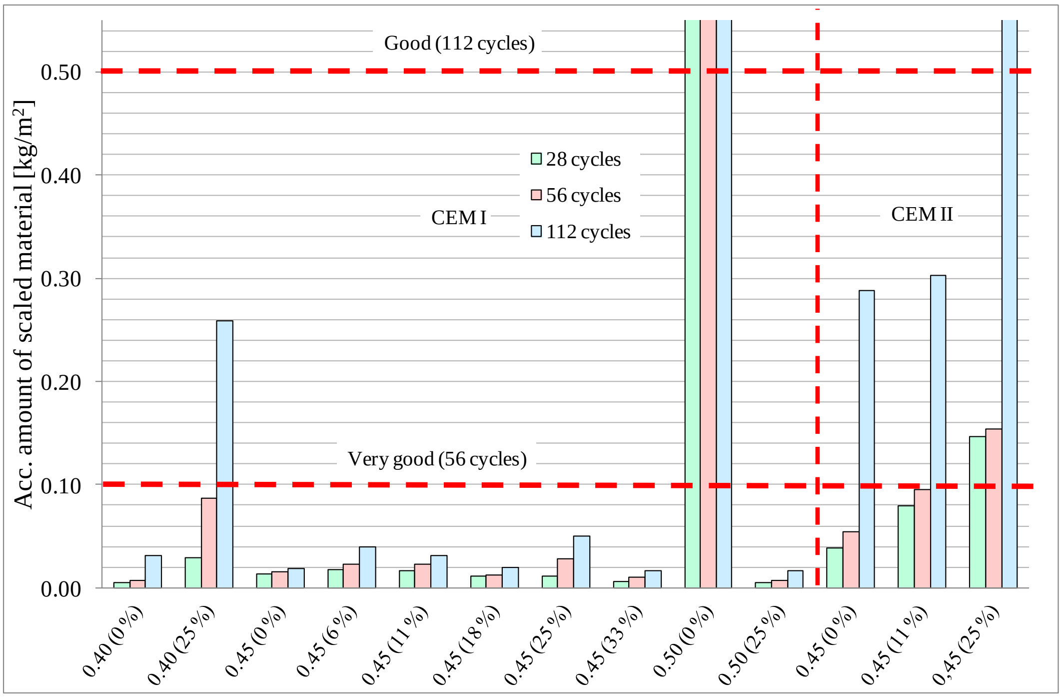

*Figure 8 – Frost resistance for concrete with 0-33 wt-% PFA of CEM I mixed with CEM I or CEM II cement and cured for 28 days before testing. Testing according to [21].*

The results in Figure 8 show that all mixes, except two, have very good frost resistance, i.e. the accumulated amount of scaled material is less than 0.10 kg/m$^2$ after 56 freeze/thaw cycles. The frost resistance for the mix with 0 % PFA and $(w/c)_{eq}$=0.50 is not acceptable and this is most probably caused by a bad air pore system even though the air content in the fresh concrete was sufficiently high (5.5 %). The mix with CEM II, 25 % PFA has acceptable frost resistance, i.e. the accumulated amount of scaled material is less than 1.00 kg/m$^2$ after 112 freeze/thaw cycles.

In Figure 8 the results from the mixes with 11 wt-% PFA of CEM I, $(w/c)_{eq}$=0.40 and $(w/c)_{eq}$=0.50, are missing. Due to a mistake the testing was started after 56 days instead of 28 days. The frost resistance for these mixes is, however, probably very good (the frost resistance for specimens cured for 56 days before testing is very good).

The frost resistance has also been tested after 56 days of curing and the result show that all mixes, except two, have very good frost resistance, i.e. the accumulated amount of scaled material is less than 0.10 kg/m$^2$ after 56 freeze/thaw cycles. The same mix that failed at testing after 28 days of curing also failed after 56 days of curing. Similarly, the mix with CEM II and 25 % PFA, $(w/c)_{eq}$=0.45 has acceptable frost resistance, i.e. the accumulated amount of scaled material is less than 1.00 kg/m$^2$ after 112 freeze/thaw cycles. The results also show that prolonged curing does not improve the frost resistance. Instead the frost resistance is slightly decreased, similar to what is observed in [18]. Furthermore the mixes with CEM II show generally somewhat lower frost resistance than the mixes with CEM I, especially with 25 % PFA. This will be further discussed in chapter 6.

The investigations show that the most important factor to create a frost resistant concrete is to create a good air pore system in the concrete. Additions of PFA have no significant influence on the frost resistance, at least for additions of up to 33 wt-% PFA of CEM I, as long as the air pore system is good. The experiences also show that the dosage of air entraining agent has to be increased, when PFA is added to the concrete, possibly due to a certain amount of unburned coal which adsorbs partly the air entraining agent. Also a certain dosage of superplasticizer has to be added to the mix.

### 4.3 Final comments – Lindvall (2011)

The general conclusion from the investigations by [22] is that concrete with additions of PFA (up to 33 wt-% of CEM I and that fulfils the requirements in [1]), *k*=0.4, gets properties that are equivalent to comparable CEM I concretes. The effects from prolonged curing (56 days) are unclear for concrete with PFA, where the performance is both improved and impaired.

## 5. INVESTIGATIONS BY CORREIA (2012)

Tomas Concrete Group has in collaboration with Chalmers University of Technology participated in a Master Thesis project, where the aim was to investigate the durability of concretes with GGBS, with special focus on frost durability. In the following sections a short review of the project is made. A full presentation of the results will be given in [24].

### 5.1 Concrete compositions and performed test

The concrete mixes tested by [24] were proportioned so as to fulfil the requirements specified in [4] for exposure class XF4, i.e. $(w/c)_{eq}$=0.45. In total four different mixes were included in the investigation (with different additions of PFA and *k*-factors):

- $(w/c)_{eq}$=0.45. No GGBS (reference mix). One mix.
- $(w/c)_{eq}$=0.45 and *k*=0.6. 25-100 wt-% GGBS of CEM I. Four mixes.
- $(w/c)_{eq}$=0.45 and *k*=1.0. 50 wt-% GGBS of CEM I. One mix.
- $(w/c)_{eq}$=0.45 and *k*=0.6. 0-50 wt-% GGBS of CEM I. No superplasticizer added. Two mixes.

Cementa Anläggningscement (CEM I 42.5 N MH/SR/LA) and GGBS from Holcim Werk Bremen (which fulfils the requirements in [2]) were used in all mixes. The workability and air content of the concrete was adjusted by additions of superplasticizer (VR – SIKA Sikament 56/50, which is polycarboxylate based) and air entraining agent (AEA – SIKA SikaAer-S, which is a synthetic tenside). The dosages of the admixtures were regulated so the air content in the fresh concrete was kept at 4.5±0.5 % or 6.0±0.5 % (one mix with higher air contents was tested). Both the VR and the AEA were added to the mixing water. The concrete has been mixed for two minutes in a Zyklos Rotating Pan Mixer before casting. The required dosage of AEA had to be slightly increased for the mixes with increasing addition of GGBS. The mix with 6.0 % air needed more than double the dosage of AEA compared to the mixes with 4.5 % air. The mixes without VR needed almost three times the dosage of AEA compared to the mixes with VR.

### 5.2 Results

Several tests have been performed on the properties of both the fresh concrete and hardened concrete. In this paper only the results from testing of the compressive strength, resistance against chloride ingress and frost attack will be presented. A complete presentation of the results will be given in [24].

*Compressive strength*

The compressive strength was determined on cubes (150x150x150 $mm^3$) after 7, 28 or 56 curing in water (+20°C). The testing was in accordance with [13]. The results from the mixes with up to 100 wt-% GGBS of CEM I are presented in Figure 9. The indexes show the amount of GGBS (wt-% of CEM I), if the air content in the fresh concrete was 6 % or if the *k*-factor was 1.0.

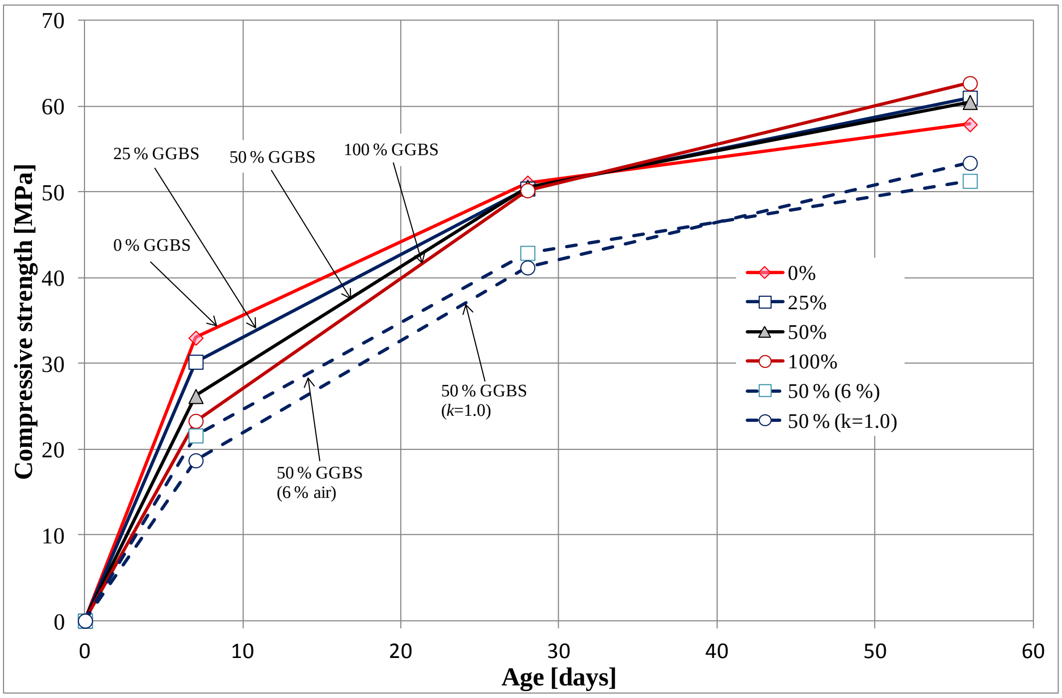

*Figure 9 – Compressive strength determined on concrete with 0 %-100 % GGBS mixed with CEM I with different curing times. $(w/c)_{eq}=0.45$. Testing according to [19].*

Figure 10 illustrates the effect of additions of GGBS on the compressive strength, where the strength before 28 days of curing is lower but after 28 days its higher for the mixes with GGBS (*k*=0.6), compared to the reference mix. At 28 days the compressive strength is similar for all tested mixes (with 4.5 % air and *k*=0.6 – the difference is approximately 1 MPa). If a higher air content (6 %) or *k*-factor (*k*=1.0) is used the compressive strength is reduced.

*Resistance against chloride ingress - $D_{RCM}$*

The resistance against chloride ingress was determined in terms of a rapid chloride migration coefficient, $D_{RCM}$, according to the method described in [20]. The results from the mixes with up to 100 wt-% GGBS of CEM I are presented in Figure 10.

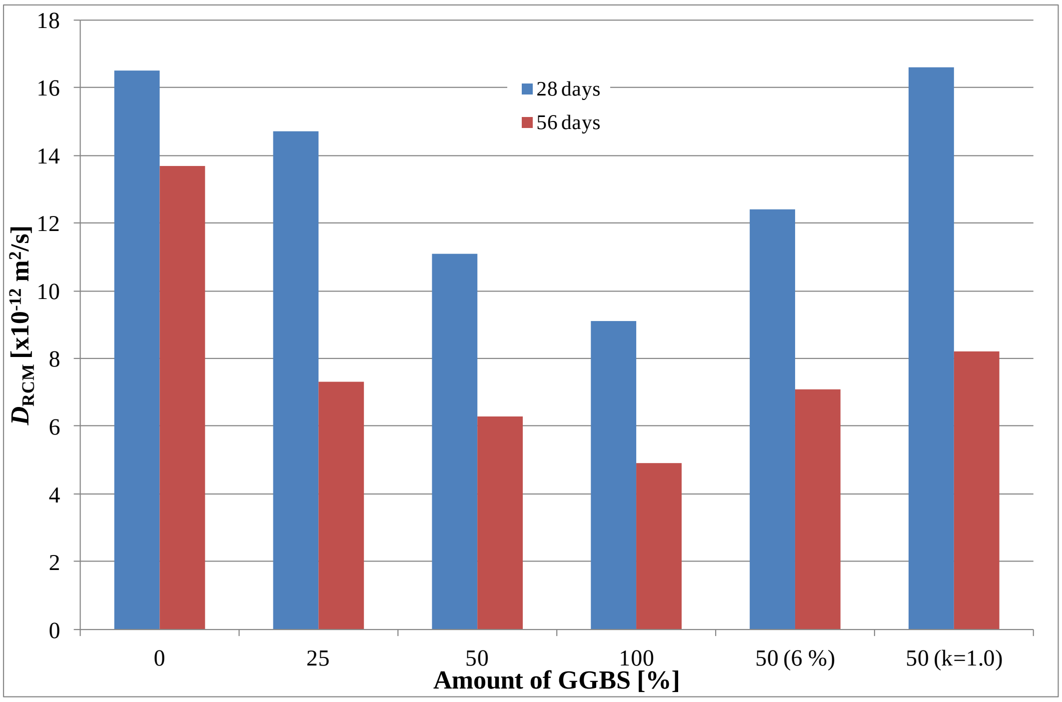

*Figure 10 – Resistance against chloride ingress determined as* $D_{RCM}$ *for concrete with 0 %-100 % GGBS mixed with CEM I with different curing times.* $(w/c)_{eq}=0.45$*. Testing according to [20].*

In Figure 11 the positive effect from additions of GGBS on the resistance against chloride ingress is clear, especially for 56 days of curing. With an addition of 100 % GGBS of CEM I $D_{\mathrm{RCM}}$ is decreased with 45 % after 28 days and 65 % after 56 days compared to the reference mix. Even with an air content of 6 % & or $k$=1.0 $D_{\mathrm{RCM}}$ is significantly lower than the reference mix.

## 5.3 Preliminary final comments – Correia (2012)

The preliminary conclusion from the investigations by [24] is that the concrete with GGBS (up to 100 wt-% of CEM I and that fulfils the requirements in [2]), $k$=0.6, gets properties that are equivalent or better compared to CEM I concrete (also with $k$ = 1.0).

# 6. DISCUSSION

The aim of the investigations presented in this paper was to investigate whether concrete with PFA or GGBS gets properties that are equivalent to CEM I concretes. The results show that this is the case (at least for additions of up to 33 wt-% PFA or 100 wt-% GGBS of CEM I and with a PFA or GGBS that fulfils the requirements in [1-2]). For some properties the performance is also improved compared to CEM I concretes, e.g. resistance against chloride ingress.

## 6.1 Strength

The measurements of compressive strength show that there are differences between the concrete mixes, both in terms of strength and strength development. Additions of PFA or GGBS influence the strength development, since the reactions of PFA or GGBS are slower than CEM I (the puzzolanic reactions of PFA or GGBS require calcium hydroxide from the cement reaction). As a consequence the strength development up to 28 days is slower for concrete with PFA or GGBS but it continues also after 56 days. Additionally the contribution from PFA or GGBS on the strength is less than CEM I, which means that the amount of PFA or GGBS that is added to a concrete must be larger than the amount of CEM I it replaces, to achieve similar strengths, which is regulated with the *k*-factors. The measured compressive strengths show that these *k*-factors are reasonable in combination with CEM I 42.5 N MH/SR/LA, but that higher *k*-factors might be appropriate for other types of cements.

## 6.2 Resistance against chloride ingress - $D_{\mathrm{RCM}}$

The measured $D_{\mathrm{RCM}}$ show that the concretes with PFA or GGBS get significantly higher resistance against chloride ingress than CEM I concretes (i.e. lower $D_{\mathrm{RCM}}$). With prolonged curing time (e.g. 56 days) the resistance is significantly improved. With additions of PFA that exceeds 10-15 wt-% of CEM I $D_{\mathrm{RCM}}$ is decreased with approximately 20 % (after 28 days of curing) and 50 % (after 56 days of curing) compared to CEM I concretes. With additions of GGBS (exceeding 25 wt-% of CEM I) $D_{\mathrm{RCM}}$ is decreased with up to 45 % (after 28 days of curing) and 65 % (after 56 days of curing) compared to CEM I concretes. The lowest $D_{\mathrm{RCM}}$ was observed for the concretes with 33 wt-% PFA or 100 wt-% GGBS of CEM I. This also means that $k$=0.4 (for PFA) or $k$=0.6 (for GGBS) are too low with respect to the resistance against chloride ingress.

$D_{\mathrm{RCM}}$ decreases with increasing age of the concrete, which is a result of that both CEM I and PFA or GGBS continues to react also after 28 days. As a result the structure of the concrete gets denser which increases the resistance against penetration of harmful substances, e.g. chlorides. As expected the effect is clearer for concrete with PFA or GGBS since the puzzolanic reactions of the PFA or GGBS continues in larger extent than the reactions of the CEM I after 28 days of age. The total amount of binder is larger in concrete with PFA or GGBS (since $k$=0.4 or $k$=0.6, i.e. the additions of PFA or GGBS are larger than the amount of cement they replace), which results in a less permeable concrete. In concrete with PFA pore blocking may also occur, where the pore system gets discontinuous, which gives a denser concrete.

## 6.3 Frost resistance

The frost resistance, which has been in focus in the investigations presented in this paper, is very good for all investigated concrete mixes (according to the requirements in [21]), also for concrete with PFA (at least up to 33 wt-% of CEM I, where the PFA fulfils the requirements in [1], $k$=0.4). At present (April 2012), no results from the testing of frost resistance of concrete with GGBS are available. Therefore only frost resistance for concrete with PFA is discussed.

The prerequisite to achieve good frost resistance is that a good air pore system has been created in the concrete, irrespective if PFA is added to the concrete or not. All investigated concrete mixes have sufficiently entrained air, by additions of AEA, so the air pore systems are acceptable (with respect to air contents and spacing factors). The frost resistance of two of the investigated concrete mixes was less good, which could be attributed to the fact that the air pore system was relatively poor, which can occur in both concretes with and without PFA.

The dosages of AEA vary between the concrete mixes, where the dosages had to be increased to achieve sufficiently high air content when PFA is added to the concrete. Similar observations are reported in the literature, cf. [23], where higher dosages of AEA were required in concretes with PFA compared to CEM I concretes. An explanation is that the AEA is absorbed by the PFA particles, where especially unburned carbon particles influence the number of "absorption sites". Another interesting observation was that, to achieve the requested air content in the fresh concrete, with reasonable dosages of the AEA, both VR and AEA have to be added to the mix. If no VR was added the dosage of AEA had to be increased to a level significantly above the recommended levels from the manufacturer. A probable explanation can be that the VR blocks or occupies the "absorption sites", which results in less absorption of the AEA that instead is available to entrain air in the concrete. Additionally there is a synthesis between the AEA and the VR (polycarboxylate based), which results in lower dosages of the AEA to achieve the requested air content in the concrete with PFA.

The frost resistance was slightly decreased for concrete with PFA, cured under prolonged time or at a higher temperature. The effects on the properties of concrete are however somewhat contradicting. On one hand the maturity and the strength of the concrete get higher, which lead to reduced porosity and water adsorption (which should improve the frost resistance), whilst on the other hand the capillary pore structure of the concrete gets finer which may lead to higher hydraulic pressures under freezing. As a consequence, there seems to be an increased risk of frost damage. The latter effect might be more dominant in the investigations presented in this paper and therefore the frost resistance is slightly reduced. This has also been confirmed by microscopic analysis of thin sections of some of the concrete mixes.

The influence of *k*-factor on the frost resistance was investigated, where the frost resistance for concrete with *k*=1.0 is slightly decreased compared to that with *k*=0.4. A higher *k*-factor means that the total amount of binder decreases in the concrete. This implies on one hand that the strength of the concretes is lower, which decreases the frost resistance, whilst on the other hand the capillary pores are getting coarser, which should result in reduced hydraulic pressures and a lower risk for frost damage. The reduced strength of the concrete might be more dominant in this case and consequently the frost resistance is lower.

There is a difference in frost resistance between concrete mixed with CEM I and CEM II, where the latter has lower frost resistance also for mixes without PFA. According to the manufacturer of the AEA that has been used is in first hand developed for the CEM I 42.5 N MH/SR/LA (since this cement normally is used for structures in exposure class XF4). There are also differences in chemical composition and physical properties between the CEM I and CEM II, which influence the performance of the AEA. Additionally the CEM II contains porous limestone powder, which may affect the water saturation and consequently result in an increased risk of frost damage.

## 7. FINAL COMMENTS AND RECOMMENDATIONS

The results from the investigations presented in this paper show that concrete with additions of PFA or GGBS (which fulfils the requirements in [1-2] and with dosages that are prescribed in [4]) has properties that are at least similar to comparable CEM I concretes. For some properties additions of PFA or GGBS also improves the performance compared to CEM I concretes.

## 7.1 Final comments

The following final comments can be given:

- **Compressive strength**, where the strength at 28 days is approximately the same for all investigated concrete mixes with Cementa Anläggningscement (CEM I 42.5 N MH/SR/LA) if $k$=0.4 or $k$=0.6 (i.e. what is prescribed in [3-4]). The strength development is usually slower for concrete with PFA or GGBS up to an age of 28 days, but continues faster after 28 days, due to the puzzolanic reactions of the PFA or GGBS, which are slower than CEM I.
- **Resistance against chloride ($D_{RCM}$)**, where the resistance generally is higher for concretes with PFA or GGBS than for comparable CEM I concretes. The results show that the resistance increases with increasing addition of PFA or GGBS (at least up to 33 wt-% PFA or 100 wt-% GGBS of CEM I).
- **Frost resistance**, where concrete with PFA gets similar resistance as CEM I concrete if the requirements [3 & 4] are fulfilled (maximum addition of PFA 25 wt-% of CEM I and $(w/c)_{eq}$=0.45). The most important factor to create a frost resistant concrete, irrespective the additions of PFA, is to create a good air pore system (i.e. sufficient air content and spacing factor). A good air pore system is created by additions of AEA with regulated dosage and with combination of VR.

## 7.2 Recommendations

Additions of PFA or GGBS have been used for a long time to alter and in some situations improve the properties of concrete. With the increasing requirements of durable structures with reduced environmental impact the interest of using PFA or GGBS in concrete has increased. However, the standards that regulate the addition of PFA or GGBS in concrete reflect the worst case, i.e. PFA or GGBS that are just meeting the requirements in the standards [1-2] are used, which means that the allowed $k$-factors and additions are conservative with regard to the durability of concrete. In the investigations presented in this paper concrete mixed with high quality PFA or GGBS was used and the results indicate that the regulations in the standards are too conservative. Therefore it is suggested that the standards should be reviewed with respect to allowed $k$-factors and additions of PFA or GGBS, to allow higher $k$-factors and additions also in rough environments.

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# Concrete Freeze-Thaw Scaling Resistance Testing
# Experience and Development of a Testing Regime & Acceptance Criteria

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## ABSTRACT

European requests for more exposure differentiation based testing and performance evaluation has called for a review of the CEN test for freeze-thaw testing (scaling). Concern regarding adequate lab vs. field relation of testing already initiated Nordic initiative related to the reviewing committee. It is considered essential to point out adequate modifications in the execution of the testing procedure – and to avoid others from being adopted. The perspective of increasing application of composite cement/binder calls for investigating potential change in bias due to change in properties development and, hence, the lab vs. field relation when testing such cement/concrete.

Also, the basis for evaluation of F-T resistance under fresh water (non saline) conditions, included as an alternative in the testing procedure is scarce and should be investigated.

**Key words:** Lab-field correlation of future concrete, different requirements, saline and non-saline environment testing, on-going CEN committee work, research in planning.

## 1 INTRODUCTION

The testing method for determination of freeze-thaw resistance of concrete in accordance with CEN/TS 12390-9 [1] is subject to review by CEN/TC 51/WG 12/TG 4. The background is a call for a testing set-up enabling expectedly more correct assessment of freeze-thaw resistance performance for “milder” exposure and requirements than under the current regime (provided in the TS). Alternative application of the main procedure is included in the TS but not adequately understood, and the same goes for the national responsibility of establishing acceptance criteria in national application documents of the concrete standard (XX[1)]-EN 206 : NA). Hence, the complexity of the testing procedure and concern to avoid inadequate local changes calls for some changes.

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[1)] *National code prefix, e.g. NS-EN 206 designates the Norwegian version*

Implicitly, the preparation of the current testing regime mainly followed on the in-situ experience of CEM I cement (XX-EN 197-1) (“Portland cement”) containing concrete. Subjecting more slowly developing properties concrete to this regime may disfavour or even disqualify adequate binder combinations. Failing to do so, may impair industry’s ability to adopt sustainable solutions [10].

The Norwegian EN 206-1 application rules offers approval by qualification testing for cement not covered by the current application rules (e.g. CEM II/B-V (or -S)) under saline conditions only, covering all the exposure classes XF2, XF3 (the latter high degree of water saturation, but no de-icer) and XF4 by the same procedure. (XF1 does not require qualification testing.). This is partly a result of the overall missing application guidelines, left to being established “in accordance with local conditions”. However, this also results from the underlying lack of lab vs. field experience when testing with water only, enabling the adoption of any acceptance criteria.

Finally, although – or because - the CEN/TS provides one reference method (“Slab test”) and two alternative methods (“Cube test” and “CF/CDF test”), all three with either saline or non-saline conditions, no specific statements are provided concerning linking of exposure class, selection of procedure or scaling/damage acceptance criteria. Though, it is not usual to include acceptance criteria in a testing standard as done in the Swedish version (Slab test only) [2].

These concerns may be satisfied by considering changes to the testing methods (incl. pre-conditioning), their application and/or test results evaluation criteria. Some modification possibly may be adopted soon, some need to follow from research. And – national authorities need to be guided for the establishing of acceptance criteria.

# 2 CONCERNS SUBJECT TO CONSIDERATION

## 2.1 General

CEN/TC 51 / WG 12 / TG 4 has been tasked with the review of the CEN/TS. Input was provided e.g. from a Nordic workshop in 2010 [11], and it is expected that a first draft will be completed during 2012 and possibly adopted in 2013. However, modifications based on possible new curing regimes need to be further investigated and will probably not be adopted on CEN level until the following revision, normally being considered every five years. Still, this does not prevent local adoption, which is why the general concerns also in this matter will be commented on, expectedly in an annex of the CEN/TS.

It is a fact that some countries or laboratories will apply the main part of the procedure but also modify certain points in order to form a more (perceived ;) relevant condition to their use. Some of these “modification options” were already pointed out in the original document as so-called “alternative applications”, in order to imply at least a sound basis for these extra “marketing needs” of F-T testing. Still, some of the modifications adopted may influence the test results in a non-foreseen way for some stakeholders and will expectedly be commented on in the annex of CEN/TS 12390-9.

The current review intends to tighten up the text at certain points, in addition to focus certain issues of significance :

## 2.2 Exposure to carbonation

Since the release of CEN/TS 12390-9, it has been acknowledged that the degree of exposure to $CO_2$ prior to F-T testing may significantly influence the degree of surface porosity and the F-T damage. The effect that may be positive to some binder combinations and detrimental to others [9] and impairs the lab/field relation as well as adequate ranking of performance based on laboratory testing. At the current stage, it is assumed that the CEN/TS will include a minimum time of exposure to $CO_2$ under “ambient conditions”.

## 2.3 Visual inspection of the test specimen

Under certain conditions, moisture from the top surface (Slab test) may permeate to the bottom of the specimen and be trapped by the bottom sealing. We have experienced that this in practice may lead to misleading scaling results and reports (even if the top surface is to be inspected with regard to amount of freezing medium). Secondly, there may be internal damages or scaling at the lower part of the specimen. Altogether, pore quality concrete may be falsely approved by this phenomenon. It is expected that the new document will provide guidance to prevent false reports.

## 2.4 Different geometry

Different geometry of the test specimen belongs to the list of “alternative application” and meets the need of e.g. testing concrete products (although a special procedure for the latter exists). It is then important to keep in mind that this may change the specimen’s heat capacity and conductivity, hence possibly also the temperature cycle of the specimen and that of the test cabinet if not adequately controlled. It is expected that this will be pointed out in the new document.

## 2.5 Cut or finished top surface

Different practices exist concerning the application of cut or finished (even formwork) surfaces. Possible effects of over-working the surface and that of the relative paste content compared to those of the bulk concrete is sometimes neglected. It is expected that this will be pointed out in the new document.

## 2.6 Deviation in curing period, moisture access and drying

Different curing period also belongs to the list of “alternative application”. However, it is not clear how this will affect the lab/field relation : Longer curing may (often reported;) imply longer water curing for slowly reacting binders, with possibly strong impact on degree of saturation and moisture exchange prior to and during F-T testing. Neither are effects of prolonged air storage on lab/field representative ranking clear, caused by carbonation or drying of the specimen. Test results on some of these issues are illustrated below but discussed more in detail by the present author in [11].

In figure 1, the CEN TS 12390-9 stages in the preparation procedure prior to freeze-thaw exposure are illustrated, with focus on the so-called "under-water-curing" period : From the demolding at 24 h (+/- 2 h), the samples are stored under water until the age of seven days. During this period, the samples are subjected to capillary suction following from on-going hydration. The extent of hydration – and capillary suction volume - during this six days period may vary significantly, depending e.g. on the reactivity (mineralogy and fineness) of the cement, level of additions (clinker replacement level) and water/binder ratio.

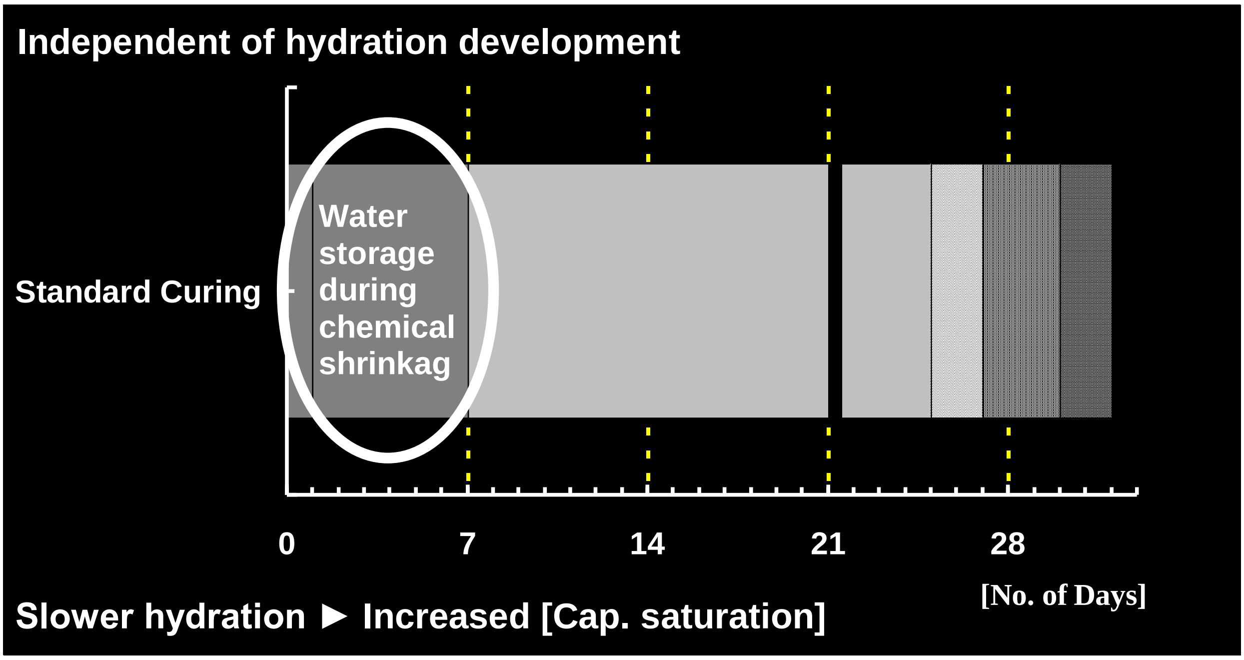

*Figure 1 – Schematic illustration of the pre-storage and preparation procedure of CEN TS 12390-9 [1], i.e. independent of concrete mix design, from [3].*

The implication of this various degree of suction is that the degree of saturation prior to the next stage, air climate chamber storage, may vary and induce variations to the succeeding evaporation conditions, controlled by diffusion and vapour (gradients) differences. The contribution of the water storage period to promote hydration (perception of "curing") is questionable : If a neutral "maturity" period is to be kept for allowing hydration, this could in most cases be provided by isolated curing, i.e. only preventing loss of initially added moisture (mixing water).

An attempt to reduce the external moisture exposure at this stage ("Plastic curing") is illustrated in figure 2, and the resulting behaviour with respect to moisture uptake during the procedural re-saturation in figure 3. The latter followed almost no difference in moisture loss during "air curing" between plastic and standard curing, although the plastic stored samples had already been cut and standard cured samples lost moisture from the lateral surfaces only. Trying to isolate the effect of early age (7d) sawing lead to substantial weight loss and re-saturation uptake ("Modified standard"). Moisture uptake took place from the top surface only in all cases. The study is extracted from [3].

Needless to say, the impact of these "alternative applications" on moisture loss during pre-conditioning and uptake during re-saturation, as well as during F-T testing and on scaling level, is substantial. The sensitivity of course varies with w/b-ratios and binder type.

At this stage of the CEN/TS, it is considered relevant to warn against these effects only : More research is needed in order to establish adequate lab/field relation for slowly maturing binders, to be incorporated in future revisions of the test procedure. The same applies to possible alternating freezing under moisture and drying in air, simulating a more field relevant moisture regime.

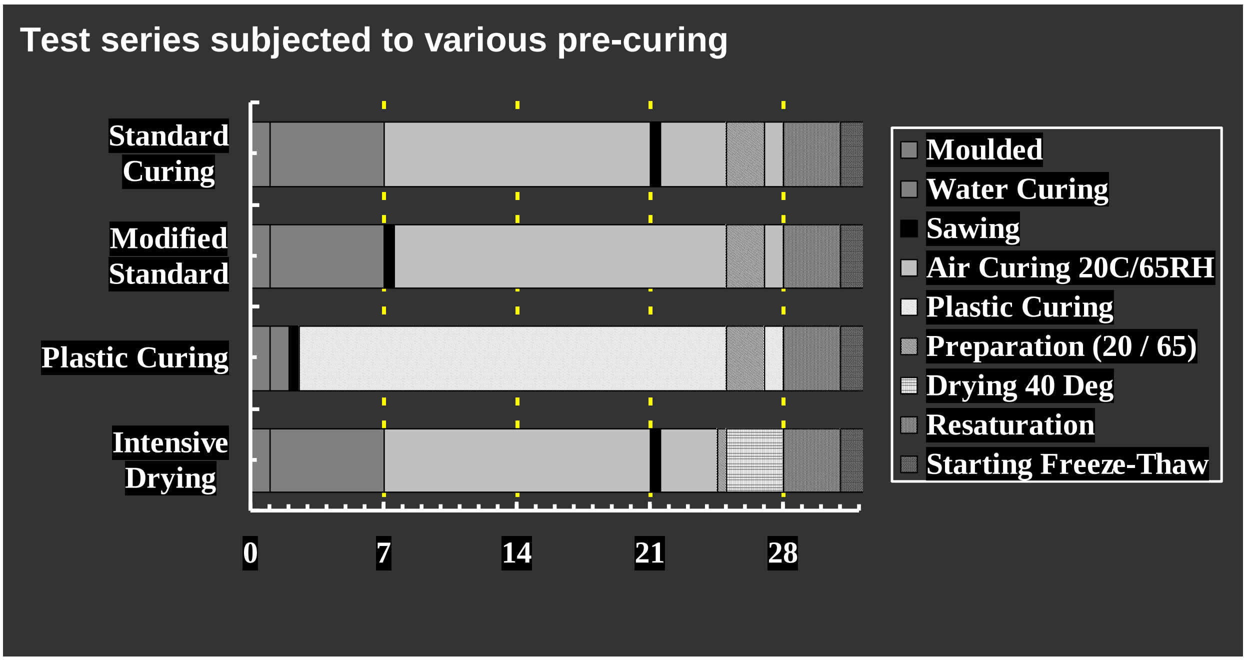

*Figure 2 – Schematic illustration of investigated pre-storage conditions [3].*

### 2.7 Different de-icing agent

The application of different de-icing agents (others than 3 % NaCl) belongs to the list of “alternative application”. Tap water and de-ionized water belong to these, but also other chemicals. Consequently, different mechanisms as well as a change of relation between temperature level and amount of freezeable moisture may apply. Even lab/field relation for XF1 and XF 3 has not been established, an essential issue for adoption of environmentally friendly binders for buildings. This belongs to future research needs.

### 2.8 Change of temperature cycle

It should be strongly warned against substantial changes of the temperature cycle, since the amount of freezing water (degree of ice formation) is not linear with drop in temperature. The ice formation is a function of the capillary pore size distribution of the concrete [4], and changing the minimum temperature may significantly impair the precision of the test. The current minimum level has been fixed to a level of low sensitivity.

### 2.9 Nos. of F-T cycles

Lower number of F-T cycles than the normally applied 56 cycles – together with differentiated acceptance criteria - probably forms the best current tool for establishing a milder regime for the evaluation of mid-western and southern European conditions. Such measures do not severely influence the basic mechanisms of F-T exposure and facilitate opportunities for local authorities of adapting the test procedure as close as possible to local needs.

## 3 CONCLUSIONS

Some tightening of the CEN/TS 12390-9 is expected to be incorporated during 2012-13, while important issues need to be further investigated before adoption.
Future ISO and CEN concrete standards are expected to be more performance oriented, in contrast to the current almost entirely specification focus concept. Within such a framework, it is essential that testing methods not only are able to rank material qualities correctly but also are capable of predicting service performance to a reasonable level of precision. This should be an important dimension for approving such testing methods.

Included in such a framework, the responsibility of national regulations to take on board local acceptance limits must be stronger integrated, compared to what we experience today.

Important modifications – partly already applied by some laboratories – fail verification with regards to effect on performance quality ranking and service life prediction.

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# Low-heat concrete with fly ash in massive infrastructures; experience from Norway on hardening phase crack sensitivity

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## ABSTRACT

As a measure to reduce the risk of thermal cracking in the hardening phase the research and practical use of concrete with larger fly ash contents have increased the last decade in Norway. Regarding “crack-control” the Bjørvika submerged tunnel projects in Oslo were a kick-off, since for the first time NPRA required both fly ash additions as well as pre-simulations of temperature and stress development. The paper attempts to give a summary on the main laboratory and field experience in Norway with the use of fly ash, in combination with stress simulations; as tools to make water-tight infrastructures without through-cracks.

**Key words:** Hardening concrete, thermal cracking, low-heat concrete, fly ash, simulations

## 1. INTRODUCTION

Hardening concrete structures are often subjected to some sort of external restraint from adjoining structural members. Under such conditions the hydration-induced volume changes of the concrete will cause stresses and there is a risk of so-called *thermal cracking*. For massive structures where hydration heat accumulates and significant temperature maxima may occur, the subsequent cooling (thermal contraction) produces high tensile stresses and cracking is the result in many cases. The cracks then go through the entire thickness of the structure (“through-cracking”) challenging aesthetics, water-tightness and durability.

As hydration heat most often is the main driving force to cracking, a sensible strategy is to apply concrete with low heat development to reduce the temperature increase in the structure. An additional tool is to use stress-simulation programs to predict the risk of cracking before casting for relevant weather conditions and execution methods. In this way the type of concrete and curing that ensure a crack-free structure can be predicted. Proper execution may involve lowering fresh concrete temperature, cooling pipes in cast structure or heating cables in adjoining structure. An example of deformations in a wall-on-slab structure during the hardening phase of the wall is shown in Figure 1.

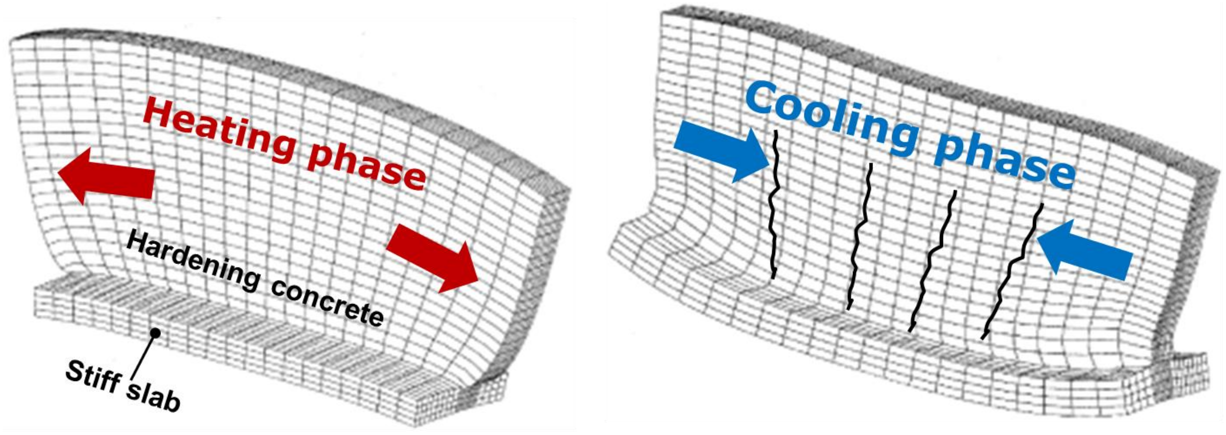

*Figure 1 – Deformation and possible though-cracking in a hardening wall (on-slab) concrete structure. The deformations are exaggerated. Based on FEM-analyses [1]*

## 2. MATERIALS PROPERTIES AND TESTING

### 2.1 General

The magnitude of stress-generation and degree of cracking risk of a hardening concrete structure depend on a number of factors, where hydration heat is one of the more important ones. FEM-simulations of the hardening concrete structures are generally done in two steps, step 1 is the temperature (and maturity) calculation and step 2 is the stress simulation. The duration of hardening phase simulations of infra-structures are normally the period from casting up to around 2-4 weeks, depending for instance on the concrete, the structure, and the season of the year. The calculated tensile stress generation over time $\sigma(t)$ in the structure is then related to the parallel development of tensile strength $f_t(t)$, and the relation between the two determines the crack risk; often expressed as a Crack Index ($C_i$):

$$C_{\mathrm{i}} = \frac{\sigma(t)}{f_t(t)} \tag{1}$$

If a simulation shows that the $C_i$ is < 1.0 the direct interpretation would be that the structure will not crack. Opposite, if $Ci$ is ≥ 1.0 then the simulation indicates that cracking will occur. However, taking the uncertainties involved into consideration (the stochastic nature of concrete properties, use of lab.-mixed concrete results for full-scale conditions, insulation of formwork, ambient conditions on-site, etc), a certain safety against cracking means that the simulated $Ci$–values should be significantly lower than 1.0 to ensure a crack-free structure “in most casted sections” of the structure.

Figure 2 shows experimental results from Temperature-Stress testing machine tests (TSTM-tests) where a given concrete has been tested three times, but at different curing temperatures (Figure 2-a). The temperature regimes are representative for walls with different thickness. The two temperature regimes with highest temperature maxima (curve 1 and 2), representing the thickest walls, generate high tensile stresses quite rapidly in the 100% restraint TSTM-specimen (Figure 2-b), causing tensile failure in both specimens after around 2.5 days. In the test with lowest temperature maximum (curve 3, representing the thinnest wall) more moderate stresses developed and it did not crack as the generated stress stayed under the tensile stress at all times, despite the fact that the restraint was 100% which an extreme case, and much higher than in most reel situations.

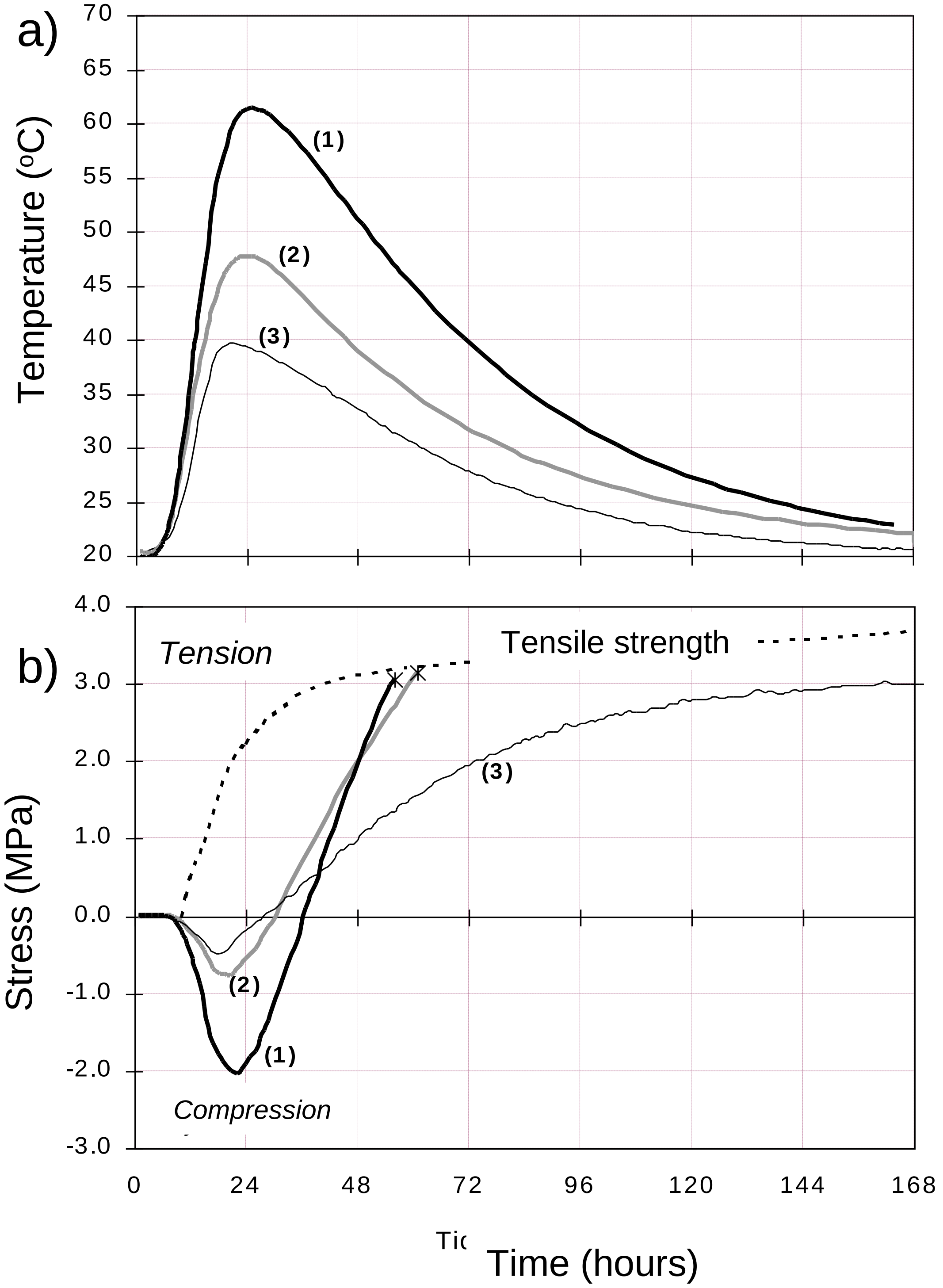

*Figure 2 – Temperature (a) and stress (b) developments for a given concrete subjected to three different temperature histories. Laboratory measurements on 100% restraint concrete beams (so-called "TSTM"-tests) [2]*

To be able to perform simulations the following materials properties has to be determined experimentally over time for the given concrete:

- Temperature sensitivity (activation energy)
- Heat of hydration
- Coefficient of thermal expansion
- Autogenous shrinkage
- E-modulus
- Creep/relaxation
- Tensile strength

Each property must be implemented into the simulation program by use of material models that are fitted to the experimental data or, depending on the simulation program, as discrete data.

## 2.2 Examples of materials behaviour

The investigations prior to the Bjørvika project (discussed later) showed that increasing dosages of the used type of fly ash (FA) systematically reduced both the hydration heat and the coefficient of thermal expansion [3]. The concretes containing FA also showed somewhat more creep than the reference [8][9]. All this is positive in reducing stresses in hardening concrete. For the given type of slag that were used the picture was quite the same, but not as pronounced as for the FA. Figure 3 shows experimental results over 2 weeks (336 hours) from tests performed with a temperature regime that are realistic for each concrete used in a wall with a thickness of 1.0 meter, 20 $^{o}$C fresh concrete temperature and 20 $^{o}$C surrounding air (Figure 3-a) [3]. The slag cement used in one of the concretes consisted of 70% slag. The reference concrete consisted of pure CEM I, while the two concretes with FA were combined with the same CEM I. All concretes had 5% silica fume of cement clinker weight. In these tests, the significant early autogenous expansion (Figure 3-b) of the slag cement concrete is notable. The explanation for this is not clear, but the phenomenon has also been seen elsewhere for the given cement type [10]. The early expansion is followed by quite substantial autogenous shrinkage. The FA-concrete shows a rather moderate and monotonic autogenous shrinkage over time. The autogenous deformation curves in Figure 3-b are deduced by using a special procedure [3] where the contribution from thermal dilation is subtracted from the measured total deformation in the test. The TSTM-tests (Figure 3-c) were performed with 100% restraint (R) in the first period until a tensile stress of 1.2 MPa was generated. At that point the closed loop deformation control was turned off, letting the stiffness of the TSTM-frame decide the restraint during the rest of the test. The restraint was then typically 30-40%. This was to avoid failure in the specimen, securing stress data over the whole period for later back-calculations where variable restraint can be handled. The stress is the net result of restraint thermal dilation (not shown here) and autogenous deformation (Figure 3-b).

Figure 4 shows the effect of FA on mechanical properties after 28 days from various research and building projects, i.e. both binder volumes and type of aggregate varies among this concretes; but all of them with water-to-binder ratios around 0.40. In hardening phase simulations it is of course the continuous development from setting which is relevant and the given 28-days results give in this regard only a picture of the properties post-hardening phase. Nevertheless, compressive strength (Figure 4-a) appears to be most systematically affected by increased FA-content, as expected. And, quite low tensile strength has been seen at the highest

FA-dosage (50% FA in Figure 4-c). Securing robust experimental data for tensile strength is recommendable as this single factor has a 1:1 effect on the calculated Crack Index.

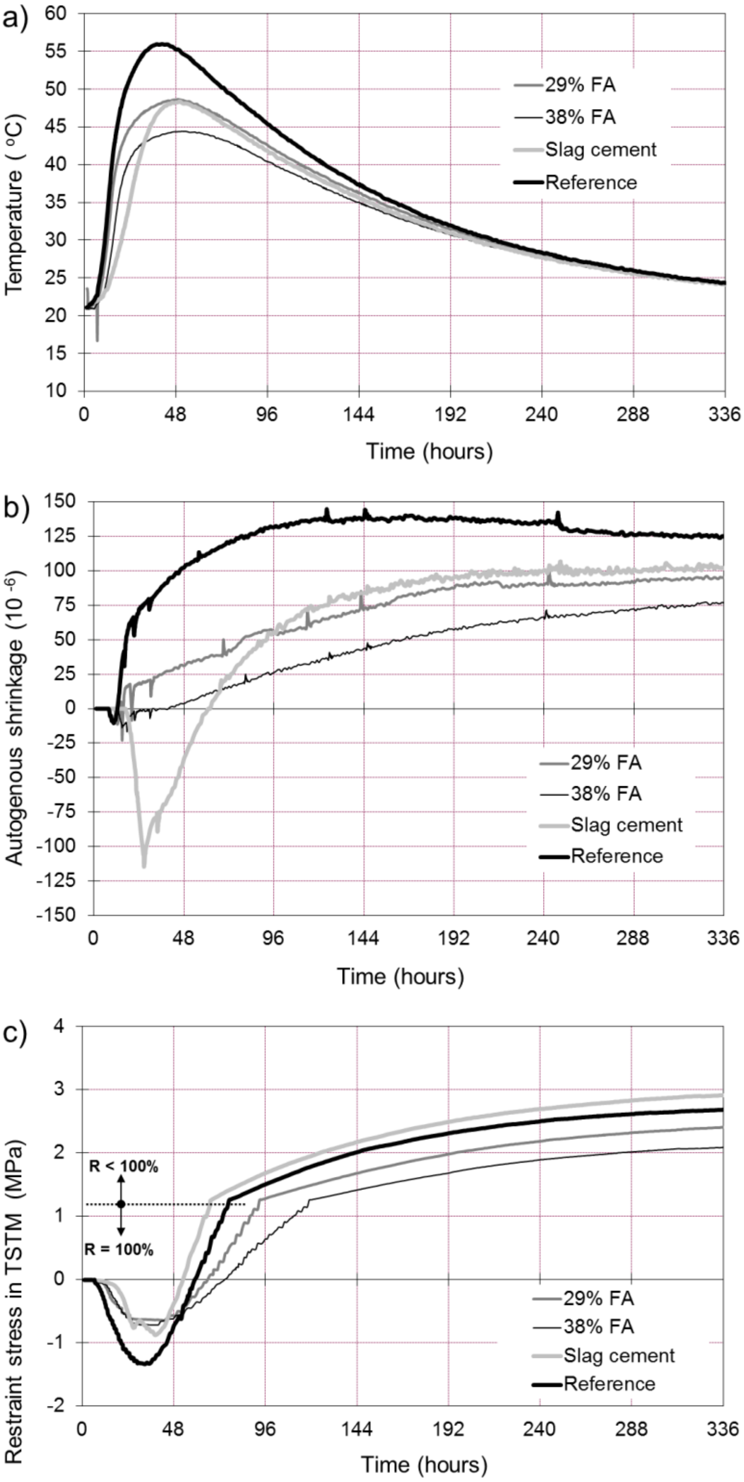

*Figure 3 – (a) Calculated average temperature development (realistic temperatures) in a 1.0 meter thick wall, based on heat data from calorimeter tests. (b) Autogenous shrinkage deduced from dilation tests performed under realistic temperatures. (c) Restraint stress from TSTM-tests performed under realistic temperatures.[3]*

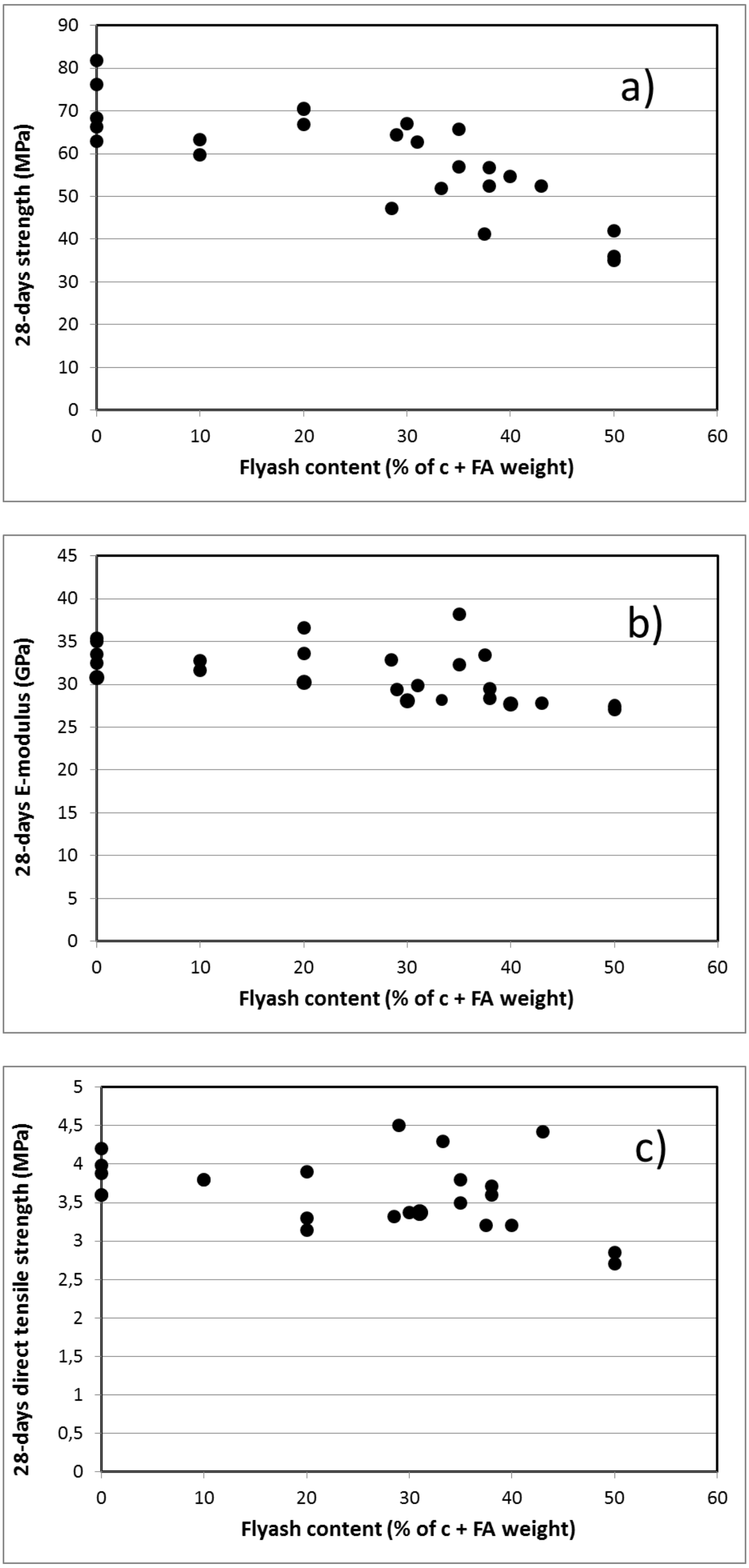

*Figure 4 – Mechanical properties after 28 days from various research and building projects*

# 3 THE BJØRVIKA SUBMERGED TUNNEL PROJECT, OSLO

## 3.1 Pre-investigations and specifications

The Bjørvika submerged tunnel in Oslo was quite special in Norwegian terms:

- it was to carry very heavy traffic
- it was the first submerged tunnel
- massive concrete culvert dimensions
- sea-water pressure from outside
- very difficult reparability

The submerged concrete culvert was to be the only barrier against the surrounding sea-water, and to obtain a water-tight and long-term durable structure "as build" was naturally of greatest importance. Considering the experience with our standard concrete specifications and our traditional binder materials, it was clear that thermal cracking was very likely to become a widespread problem. The location of the Bjørvika submerged tunnel project is sketched on the map in Figure 5. The tunnel has two driving lanes in each direction and the total width of the tunnel varies from around 28 m to around 42 m.

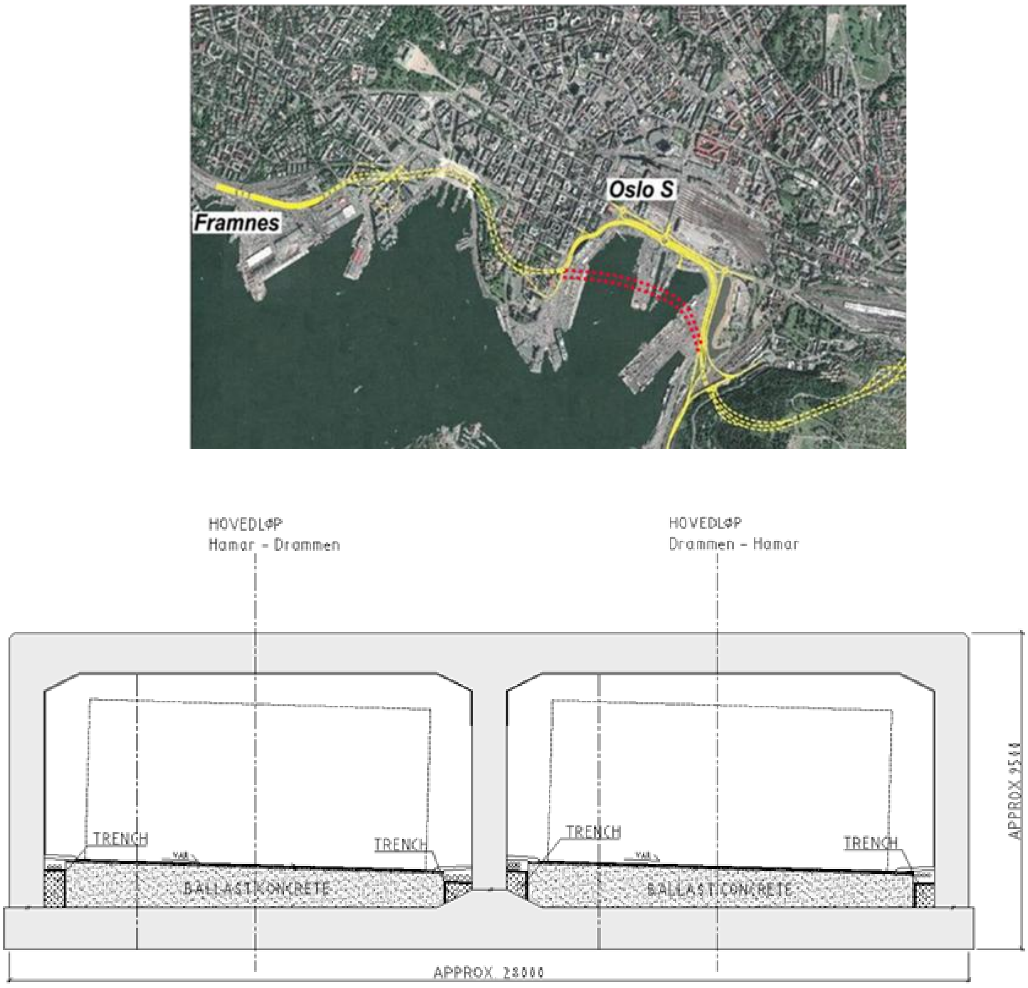

*Figure 5 – Upper figure: Location of the Bjørvika submerged tunnel project in Oslo (dotted lines over sea). Lower figure: Typical cross-section of the concrete culvert.[5]*

NPRA, being the client of the project, carried out a pre-investigation programme to seek for alternative binder combinations with possible improved properties (start around 2001). Variables in this investigation were cement type, different additions of either FA or slag, slag cements, as well as silica dosage. The most promising binder combinations from the tests (and temperature/stress calculations) on hardening phase properties were investigated further in durability tests (chloride migration, electrical resistivity, freeze-thaw). Full-scale tests were also performed to investigate, among others, fresh concrete/execution properties. All results were reported and compiled in [3]. The Bjørvika project was separated into three contracts, and based on the pre-investigations the following (key) specifications were given with regard to minimise thermal cracking in the hardening phase, and to secure durability:

***Concrete mix-design:***

- Cement, CEM I (52.5 or 42.5)
- 23-40% fly-ash (FA) addition of binder weight, fabricated in Denmark, efficiency factor $k_{fa}$=0.7
- 4-8% silica fume (s) of OPC-weight. Efficiency factor $k_s$=2,0
- mass ratio $w/(c+2s+0.7FA) \leq 0{,}45$
- non-alkalireactive aggregate
- slag or FA cement could also be used if similar/better properties were documented

***Documentation of chosen concrete(s):***

- Hardening phase property development; all relevant properties (as listed in Section 2.1)
- Full-scale test: Part of cross-section in full scale including water-stop (large trial cast) and a smaller wall (small trial cast). Test on fresh concrete properties, temperature measurements, drilling of cores for casting quality control and durability tests.
- Durability, accelerated lab. tests (not dealt with here, but treated for instance in [4])

***Evaluation of crack-risk by simulations***

- Temperature and stress simulations of all casting sections, to be reported minimum 2 weeks before casting
- The simulations shall show that the chosen concrete and execution method gives a crack index $C_i$ not above 0.75
- Measurements of temperature development in cast sections, and comparison of temperature measurements to the pre-simulations

### 3.2 Contracts and chosen concrete and execution methods

The project as a whole was separated in three contracts:

*- West side (Festningstunnelen), contractor NCC AS:*
This part consisted of a connecting culvert (in deposits under sea-water level), and also connections to existing tunnel and other existing road system. Many different structures with various complexity and different restraint conditions.

*- Submerged tunnel, contractor Arbeidsfelleskapet Bjørvika (job fellowship Bjørvika consisting of Skanska Norge AS, BAM and Volker Stevin):*
Five concrete culvert elements, each 112 m long, were built in a dry dock in Bergen and floated to Oslo, and then submerged to the bottom of the sea. Each element was cast in sections of 22.5 m. All wall sections were restraint by the older bottom slab.

*- East side (Sørenga), contractor AF Gruppen Norge AS:*
This connecting concrete culvert tunnel was built with diaphragm walls as temporary support to establish the building site; lying in deposits under sea-water level. The outer walls of the permanent concrete culvert were built as contact cast between top slab, bottom slab and diaphragm walls, i.e. high restraint conditions. The contract also involved connections to existing road system.

For the different contracts, typical wall thicknesses, chosen FA content in the concretes and execution methods are given in Table 1. Slab thicknesses were typically 1.2-1.4 m. The criteria $C_i \leq 0.75$ from the stress simulations were the basis for choosing the necessary amount of cooling pipes or ice. Ice substituting parts of the mixing water reduces the fresh concrete temperature. Cooling pipes reduces the temperature increase in the hardening structure. Both measures leading to less temperature difference between the hardening and restraining structure, lowering the crack-risk ($C_i$).

For the submerged tunnel contract the cement-producer Norcem AS started to produce a special project-cement with 32% FA. In the east and west side contracts a cement of type CEM I was used in combination with separately added FA.

*Table 1 – Key-data relevant for avoidance of thermal cracking*

| Contract | Typical wall thickness | Flyash content in concrete | Execution method |
|---|---|---|---|
| West side | 1,0 m<br>(variable) | 40% | Cooling pipes |
| Submerged tunnel | 1,0 m | 32% | Cooling pipes |
| East side | 1,0 m | 40% | Ice as part of mixing water |

## 3.3 Experience with simulations and crack-risk

For the submerged tunnel contract a report was finalized in 2010 summarizing the experience with crack-control [5]. And, a joint seminar involving all contracts, dealing with the same topic, was held the same year [6].

The general experience is that the used FA (low-heat) concretes and accompanying simulations to a large degree contributed to very little cracking in the cases where the planned countermeasures (cooling pipes or ice) worked as intended. Considering the general high restraint situations and large dimensions of the structures very few through-cracks occurred, and to a much less extent than could be expected if the traditional concrete specification had been used.

However, in all projects it appears that the initial simulations under-estimated the crack risk for the first sections that were produced. This was seen as the simulations showing $C_i$-values $\leq 0.75$ while moderate cracking was observed on-site meaning that $C_i$ really was around 1.0. The main reason for this discrepancy was probably due to the fact that splitting strength was used in the calculation of $C_i$ instead of using direct tensile strength data. When the concrete reaches a certain maturity (as the case is during the critical cooling phase) the splitting strength is seen to become significantly higher than direct tensile strength (around 20-30% higher at direct tensile strength levels of 3-4 MPa [7]). Consequently, the risk of cracking will be underestimated in simulations using splitting strength data in the calculation of $C_i$.

In the submerged tunnel project "calibrated simulations" were performed in the following taking direct tensile strength and observations on-site into consideration. The initial simulations showed that extra countermeasures were not necessary, while the calibrated simulations now showed (naturally) that actions had to be taken to bring the $C_i$ down to below 0.75. It was shown by the simulations that one row of cooling pipes along the centre of the wall was able to bring the calculated $C_i$ below 0.75. Using the "calibrated simulations" and chosen amount of cooling pipes no cracks developed in any section were the cooling pipes worked as intended. Totally 21 of 30 sections were executed with cooling pipes. Cooling pipes were installed only in the two outer walls, and not in the mid wall that was not to be exposed for sea-water pressure. An advantage in the dry dock work with the submerged tunnel was the number of very similar casting sections. The simulations were also updated with hydration heat data from several 1 $m^3$ on-site semi-adiabatic calorimeter tests, see Figure 6. The hydration heat varied markedly over time probably according to cement batch and storage time. The average heat of hydration (at 300 maturity hours) for the measurements taken was 288 kJ/kg, while min./max.-values were 264/320 kJ/kg. Experience from the on-site work (calorimeter tests, measured concrete temperatures from previous sections, effect of weather conditions) was implemented in succeeding simulations and due to the relatively invariant geometry the drawn structural configuration in the simulations program could be reused to a large extent.

*Figure 6 – On-site 1 $m^3$ semi-adiabatic calorimeters [5]*

In the two other contracts (west side and east side) similar observations were done in the way that simulations indicated that cracking was not likely to occur while on-site it was observed some cracking. The reason for the discrepancy was probably the same as for the submerged tunnel contract (i.e. mainly that splitting strength was used, and not the direct tensile strength). For the east side contract, using ice as part of the mixing water, the discrepancy meant that more ice had to be added (i.e. lower fresh concrete temperature) than the simulations showed. For the west side the implication was that more cooling pipes had to be used than indicated by the simulations.

In all the three contracts discussed above, 2-dimensional (2D) simulation programs were used. For a structure with a low length-to-height ratio (for instance typically for concrete culvert casting sections) a 2D-program generally gives somewhat higher calculated maximum stress than a full 3D-simulation. Some numbers have been given in the past regarding the difference between 2D and 3D, but the issue will not be further dealt with here as the picture is presently not entirely systematic, among others because of dependence of also other factors than merely the length-to-height ratio. Nevertheless, assuming all materials and climatic data perfectly implemented in programs, there should be a build-in conservative estimate for crack-risk for culvert sections when using 2D-simulations. This issue should be investigated further in the future.

## 4 LATER DEVELOPMENTS, POST BJØRVIKA

Start of construction work in the Bjørvika projects was in 2005, with finalization in 2010. The experiences with “high volume FA concretes” (up to 40% FA) in the Bjørvika projects were generally very good as regard to fresh concrete properties (after dealing with some problems with obtaining a stabile air entrainment), reducing/eliminating thermal cracking and durability parameters. Those involved have embraced the “new technology”, involving the availability of separately deliverances of FA.

The project-cement with 32% FA (CEM II/B-V) made for the Bjørvika submerged tunnel contract, as mentioned, was also used in some concurrent and succeeding projects due to its good reputation. Norcem AS then replaced this cement with a more all-round and commercially available cement with 20% FA (CEM II/A-V), and has continued to deliver separate FA for extra additions in projects with special focus on avoidance of thermal cracking in massive structures. The cement clinker in the two mentioned CEM II cements was originally a high strength cement CEM I of strength class 52.5 according to EN 197-1, while the todays CEM II/A-V is in strength class 42.5. For additional dosages of FA there is a further reduction in early strength, including the 28-days strength, but increased strength gain after 28 days. This issue should always be considered in the planning and production on-site (contractor responsibility) and in the decision on the adequate control age for characteristic strength (client decision, in dialogue with the contractor).

Before the production of the project-cement (32% FA) from Bjørvika was stopped, it was also used in the concrete forming the culvert structure “Skansenløpet betongtunnel” in Trondheim. Here 0.8 meters thick walls were cast on bottom slabs of 0.8-1.5 meter thickness. This concrete showed very good performance with regard to low cracking tendency even though there were no special actions taken to avoid cracking except maybe that the concrete was made with a rather low total binder volume.

For wall thicknesses around 0.4 m the present available FA cement (20% FA) is claimed to provide crack-free structures to a larger degree than seen before for CEM I-based concretes.

For special structures with thickness of around 1.0 m NPRA has now several times specified “low heat” concretes with FA-content of 33-40%.

In the on-going road-projects east of Trondheim (E6 Trondheim-Stjørdal) temperature and stress simulations, supported by experimental tests, are used actively in the choice of concrete proportions and fly ash dosage.

## 5 HEAT RELEASE PR. KG BINDER VS. ADIABATIC TEMPERATURE RISE

As mentioned, after the Bjørvika projects a new commercial "all-round" cement with 20% FA was released from Norcem (ANL-FA cement CEM II/A-V), having lower hydration heat than our traditional CEM I cements, however it is far from low-heat according to Standard terms. NS-EN 197-1 gives the term "low-heat" for cements with a characteristic heat release after 7 days ≤ 270 kJ/kg.

The ANL-FA cement (20% FA) has in several projects been used in combination with extra FA added at the mixing plant. For such mixes we really may start to talk about "low-heat binders". Some hydration heat data (after 7 days) from various research and road projects are shown in Figure 7. The figure shows the total FA-content in the concretes. It appears that the total FA-content must be rather significant before we can denote our mix truly low-heat according to the limit 270 kJ/kg, which also appear to be about an upper limit to secure sufficiently low heat release to avoid cracking (without any other measures) in wall-on-slab structures where the walls have thicknesses around 0.8-1.0 meter. Considering the temperature development in a structure, the most relevant unit is really not the *heat release pr. kg binder*. The "adiabatic temperature rise" for a given concrete is, however, better as it includes proportioning issues such as binder volume and type (density, heat capacity) of aggregate. Maybe it would be sensible to establish "heat classes" with regard to adiabatic temperature rise for a given *concrete* instead, which then could be connected to field experience on cracking tendency (typical structures, concrete thickness, restraint conditions, season, countermeasures) as a rough guideline in the choice of concrete part materials and proportions for new projects. In this regard, the adiabatic temperature rise after around 2 days is an even more relevant "parameter" than the adiabatic temperature rise after 7 days when it comes to what maximum temperatures will occur in a 0.8-1.0 m thick concrete structure. Figure 8 shows the adiabatic temperature rise after 2 days (based on the same data as Figure 6).

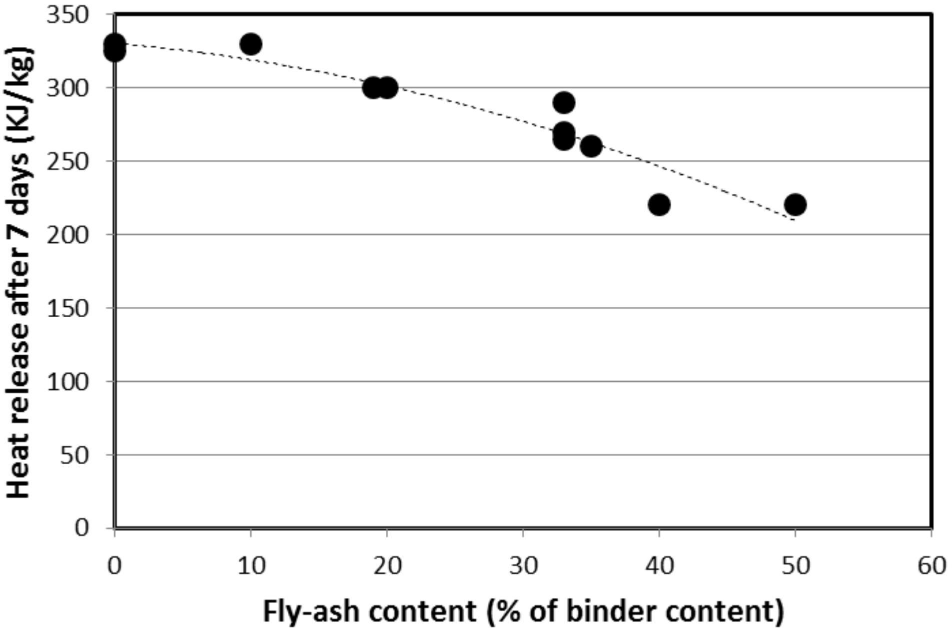

*Figure 7 – Accumulated heat release after 7 days maturity time pr. kg binder as a function of total FA-content. Data from various research and road-infrastructure projects.*

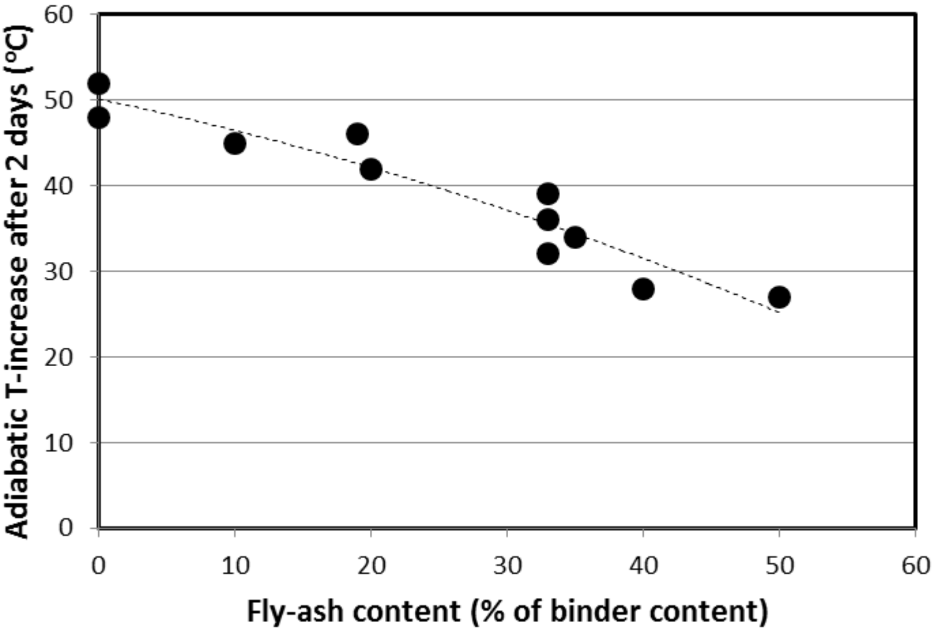

*Figure 8 – Adiabatic temperature increase after 2 days as a function of total FA-content. Data from various research and road-infrastructure projects (based on the same data as figure 6).*

## 6 FINAL REMARKS

A decade ago CEM I-based concretes were predominant in Norway for use in infrastructures, having a significant heat release, high early strength, and associated high thermal cracking-risk in massive structures. From then on there has been a development towards binders containing FA with reduced heat release and lower cracking tendency. The Bjørvika projects were a kick-off in this regard.

Even with reduced cracking tendency extra countermeasures may still be required on-site to secure a fully crack-free structure. Simulations can detect such need and also quantify the necessary magnitude of countermeasures.

Several properties control the thermal cracking tendency of concrete structures, i.e. not only heat release and the associated temperature rise. Simulations require a quite extensive test program to determine the time-development of the involved concrete properties. In simulations of the Crack Index it is shown that it is strongly advisable to use direct tensile strength data as basis and not splitting tensile strength.

A close dialogue between the operator of the simulation program and the building site is a great advantage; in this way on-site observations and updated heat data can be incorporated, and the execution method can be refined if necessary. Simulations are costly and require special competence, and should be specified only in special projects. In Norway today quite few possess the knowledge on how to perform such simulations.

Further materials research on the topic is presently on-going within the Norwegian research project COIN (www.coinweb.no), involving also the making of a Norwegian version of the Swedish simulation program ConTeSt Pro. The COIN-version of the program will be fed with updated materials data for relevant concretes of today. The program will be named CrackTeSt-COIN and courses directed towards the industry will be given. The hope is to broaden the practical use of simulations as a tool to predict and control temperature, restraint stresses and crack-risk of concrete structures.

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# Thirty Five Years of Experience with Slag Cement Concrete in Canada

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## ABSTRACT

Since its introduction into the Ontario market in 1976, partial cement replacements with ground granulated blast-furnace slag (slag cement) have been used extensively concrete placed in severe durability exposures in lieu of specialty Portland cements including low-heat cements, low-alkali cements and sulphate resistant cements. It has been found to greatly improve resistance to chloride ion penetration from both marine and de-icing salts. Based on aggressive laboratory test methods, resistance to de-icer salt scaling has been of concern to highway agencies at high cement replacement levels, but much of this can be attributed to poor finishing and curing practices. Experience in Ontario with replacement levels typically in the 20-35% range is that slag cement concrete is resistant to freezing and thawing, carbonation and provides increased resistance to chloride ingress. When used at 35-60% replacement, slag works well to prevent sulphate attack and deleterious alkali-silica reactions. Recently it has been found that slag works synergistically with silica fume cements and cements having up to 15% interground limestone in providing early strength and durability.

This paper summarizes both laboratory data and field experience on the performance of slag cement concrete in the Canadian climate.

**Key words:** Slag cement, durability, chloride resistance, ASR, sulphate resistance.

## 1. INTRODUCTION

### 1.1 General

Ground granulated Iron blast-furnace slag has been used in cementitious binders to produce concretes for over 120 years in Germany and later in much of Europe. In the last 60 years, use of slag has spread to Australia, the Pacific Rim, North America, and Africa. In Canada, the first major use of separately ground slag as a supplementary cementitious material was in 1976 with the opening of the Standard Slag Cement plant in Fruitland (now Lafarge), Ontario. The replacement level of portland cement by slag depends on both climate and application. While slag can be interground in blended cements such as CEM III/A or CEM III/B, it can also be added as a separate ingredient in concrete. In North America, slag is almost exclusively added as a separate ingredient at concrete plants (Hooton 2000).

Granulated blast-furnace slag has been used since the late 800s, but its modern use as a separately added cement replacement was pioneered in South Africa about 60 years ago. This concept then spread to the U.K. (1960s) and Canada (1970s) and then to the U.S.A. (1980s). In the late 1990s there was a large increase in the amount of separately ground granulated slag available in the coastal and central parts of the U.S.A. and annual use since then has been in excess of 3 MT (plus approximately 1 MT in Canada). However, due to transport costs, it is mainly used in states/provinces with steel mills or near coastal areas.

Blended cements, made by intergrinding granulated slag together with portland cement clinker, tend to dominate the market in Australia, Germany, and other European countries. Blended cements reduce the need for a second silo at the concrete plant, but do not provide the flexibility to change replacement levels for multiple applications or for cold and hot weather concreting. While blended cements allow the producer to optimize gypsum additions for set control and early strength, both the ASTM C989 and CSA A3001 standards also allow intergrinding of calcium sulfate with slag. While both ASTM and CSA have standards for blended cements, until recently no slag blended cements have been produced in north America. However, with increasing pressure on the cement industry to reduce its point source $C0_2$ emissions, the use of blended cements will likely increase.

### 1.2. Slag replacement levels

When separately ground slag was first introduced in Ontario, Canada in 1976, replacement levels were quite conservative: 20-25% in summer and 15-20% in winter. After over 35 years of industry use, normal replacement levels for specified strength concrete range from 20% to 40%.

Higher levels of slag are being used for special requirements, such as 50-75% for mass concrete, and up to 90% in cemented mine paste backfill. For sulphate resistance, (Hooton and Emery 1990), typically 50% replacement is sufficient to obtain equivalent performance to a sulphate resisting portland cement (CSA Type HS), and 35% replacement for moderate resistance (CSA Type MS) regardless of the $C_3A$ content of the portland cement. For control of alkali-silica reaction, 50% slag was successfully used in a series of dams in Ontario (Hooton et al 2000) and various percentages are allowed under CSA A23.2-27A depending on the reactivity of the aggregate and the exposure conditions.

## 2. EFFECTS OF SLAG ON DURABILITY

### 2.1 Modifications to pore structure and composition

Almost all properties of concrete are governed by the volume, size distribution, and connectivity of the pores in the cement paste. The initial porosity consists of the space originally occupied by water in fresh concrete (this is fixed by the water content) so use of well graded aggregates and water reducing admixtures can be used to reduce the required paste content at a given W/CM. Porosity and connectivity of capillary pores diminishes with lower W/CM and increased maturity. The C-S-H hydrates are in themselves porous at a nano-level, as C-S-H is a layered structure; but except for creep and shrinkage issues, we are more interested in the larger capillary pore system for strength, permeability, and durability. A review by Hooton et al (2009) found that slag had no effect on drying shrinkage. Drying shrinkage of 75x75x300mm concrete prisms made at W/CM = 0.55 and 300 kg/m$^3$ cementing materials, and 20mm dolomitic limestone coarse aggregates are shown in Table 1 after 7 days moist curing.

*Table 1. Drying shrinkage of concrete with different slag replacement levels of Portland cement (50% rh at 23 $^o$C).*

| Cement Type | 7 days | 28 days | 56 days | 91 days |
|---|---|---|---|---|
| Type I | 0.02% | 0.03% | 0.04% | 0.04% |
| Type I + 25% Slag | 0.01% | 0.03% | 0.04% | 0.04% |
| Type I + 50% slag | 0.01% | 0.02% | 0.03% | 0.04% |

When slag dissolves in alkaline pore solutions, it then forms secondary C-S-H, that fills in some of the capillary pore space left by the prior hydration of the portland cement fraction, helping to make a discontinuous capillary pores. As well, slag helps decrease the porosity of cement-aggregate interfaces in concretes. In addition, the C-S-H formed from slag hydration typically incorporates alumina (C-A-S-H), and has a lower C/S ratio, both of which contribute to increased chloride and alkali binding capacity (Hooton et al 2010). More detailed explanation of the effects of slag on composition and microstructure are provided in Lothenbach et al (2012).

During mixing, the concentration of cement grains near aggregate surfaces is reduced, resulting in porous zones of up to 10-20 um thick adjacent to aggregate surfaces. Often this porous interfacial transition zone (ITZ) in the paste around aggregates is observed to contain enhanced levels of sulfoaluminate hydrates and calcium hydroxide, usually in the form of large crystals. The porous ITZ reduces strength and allows increased rates of fluid penetration.

Grains of supplementary cementitious materials such as slag near these transition zones react (often later) to fill densify the ITZ by forming more C-S-H). This results in improved concrete strengths and reduced permeability and ionic diffusion rates.

## 2.2 Reduction in Fluid Penetration Resistance

Since most forms of deterioration of reinforced concrete structures result from ingress of water or ions dissolved in water, the resistance to ingress of these fluids through the capillary pore system is important for provision of durability. Permeability and diffusion will be reduced as the capillary pore volume is reduced (by lowering the water content of the mix) and a from development of a discontinuous capillary pore structure (by lowering, the W/CM, use of SCMs such as slag, and by curing the cover concrete). The secondary hydration products of slag help block capillary pores and reduce the porosity of the interfacial paste-aggregate transition zones (ITZ), resulting in much lower permeability and diffusion coefficients than plain Portland cement concrete. This is shown in Table 2 for both water permeability and the

ASTM Cl202 (AASHTO T277) rapid chloride permeability coulomb values (Bin-Ahmad 1991; Hooton 1993).

*Table 2. Effect of slag on water permeability and ASTM C1202 coulomb values for concretes of equal W/CM and initial water content (Bin-Ahmad 1991).*

| Slag % | Water | W/CM | 91-day Strength (MPa) | RCPT (coulombs) | Permeability To Water ($10^{-13}$ m/s) |
|---|---|---|---|---|---|
| 0 | 200 | 0.45 | 35.8 | 5200 | 10.1 |
| 25 | 200 | 0.45 | 42.7 | 2450 | 5.4 |
| 50 | 200 | 0.45 | 42.8 | 1020 | 2.3 |

This reduction in penetrability of aggressive fluids into concrete is of prime importance for resistance in all durability exposures.

### 4.4. Sulphate Resistance

In addition to reduced penetration of sulphate ions, the typically high slag replacements dilute the $C_3A$ content of the cement and reduces the $Ca(OH)_2$ content of the hydrated paste fraction of concrete.

The beneficial effects of slag in reducing sulphate expansion and deterioration are well known. Data for a Canadian slag are shown in Figure 1 (Hooton and Emery 1990). However, the as the $Al_20_3$ content of the slag rises above approximately 11%, the level of slag replacement required to impart sulphate resistance rises as well. With high alumina content slags, the alumina appears to compete for the calcium sulphate added to the Portland cement to control set, and can result in under-sulphated binder systems that form more residual monosulphate (at the expense of ettringite). Then when exposed to external sources of sulphate, the monsulphate is converted to ettringite, resulting in sulphate attack. With such high alumina slags, calcium sulphate can be interground with the slag, resulting in improved sulphate resistance. The ASTM Cl012 mortar test is used in both Canada and the USA to evaluate sulphate resistance of cementitious binders, with an expansion limit of 0.10% at 12 months for high sulphate resistance, and 0.10% at 6 months for moderate resistance (CSA A3001 and ASTM Cl157).

Together with the mortar bars cast by Hooton and Emery (1990), concrete cylinders were stored in 3000 mg/L sodium sulphate solutions for the first 8 years, then in 50,000 mg/L sodium sulphate solutions, and are still in test. After 35 years, the concretes made with high $C_3A$ (12.3%) portland cement replaced with 45, 65 or 72% slag remain visually undamaged while moderate and low $C_3A$ Portland cements have been completely destroyed.

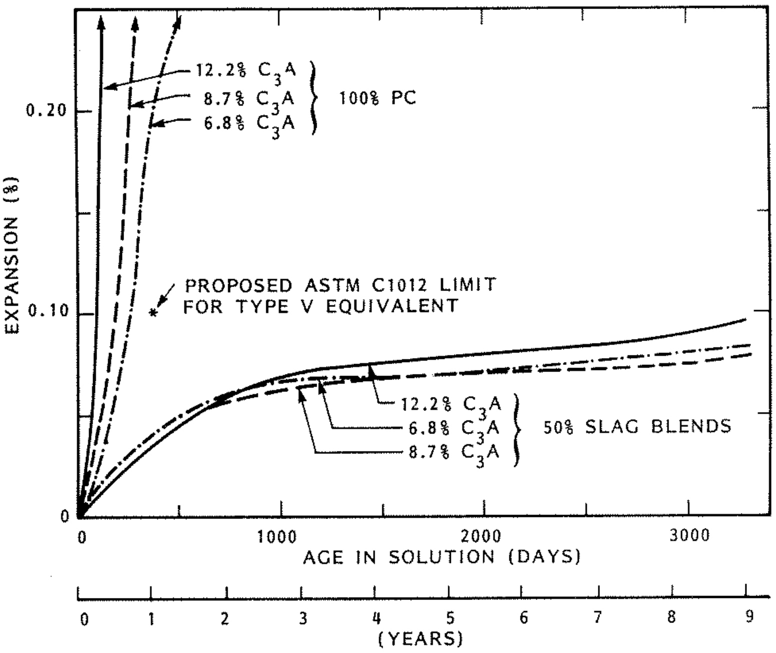

*Figure 1. Reduction of ASTM C1012 mortar bar sulphate expansions from use of 50% slag replacing cements of different $C_3A$ (Hooton and Emery 1990)*

The potential for the low-temperature thaumasite form of sulphate attack can also be mitigated when sufficient levels of slag are used (Higgins 2003) including Portland-limestone cements such as allowed in CSA A3001, ASTM C595 and CEMIIA-L (Hooton et al 2011).

Slag is also beneficial in preventing damage due to delayed ettringite formation (DEF) for concrete subjected to temperatures in Excess of 65°C at early ages (Ramlochan et al 2004).

## 2.5. Resistance to chloride penetration and reinforcement corrosion

As stated earlier, even at modest replacement levels, slag will act to reduce the rate of chloride penetration into concrete. As long as sufficient hydration is achieved, higher slag levels will offer more improvement. Non-steady state chloride diffusion values from NORDTEST NT492 are shown in Table 3. In addition, due to continued long-term hydration, the diffusion coefficients will continue to improve with time. As well, slag will result in increased levels of chloride binding, likely due to formation of more chloroaluminate compounds (Thomas et al 2012) and from the lower Ca/Si ratio of the C-S-H developing from the slag (Hooton et al 2010). The reduction in pore connectivity can also be detected by higher electrical resistivity of slag concretes, as shown in Table 3 (Hooton and Karkar 2012).

*Table 3. Chloride penetration resistance and resistivity of concretes (330kg/m$^3$ binder)*

| | ASTM C1202 (Coulombs) | | NT492 Dnns $10^{-12}$ (m$^2$/s) | | Resistivity (ohm-m) | |
|---|---|---|---|---|---|---|
| Concrete W/CM and % Slag | 35 Days | 56 Days | 35 Days | 56 Days | 35 Days | 56 Days |
| 0.50, 35% Slag | 994 | 877 | 5.7 | 4.9 | 139.8 | 150.9 |
| 0.50, 0% Slag | 2456 | 2205 | 13.6 | 11.1 | 55.3 | 65.2 |
| 0.45, 50% Slag | 726 | 581 | 4.8 | 3.7 | 201.2 | 251.4 |
| 0.40, 50% Slag | 784 | 632 | 3.2 | 3.0 | 188.3 | 226.4 |

The result of all these factors is that with slag concrete, the time to depassivation of embedded reinforcing steel is significantly extended (provided that there is sufficient depth of cover and the concrete has been properly designed, compacted, and cured). In Table 4, a portland cement concrete (Concrete A) was compared with a 25% slag concrete (Concrete B) at W/CM = 0.40. As well, a 0.30 W/CM high performance concrete was cast with 40% slag and 8% silica fume (McGrath and Hooton 1997). Slabs were moist cured 5 days and then air cured to 56 days. After curing, they were subject to a chloride ponding test (exposed to 5 M NaCl solution at 40°C for 120 days) then profile ground to obtain a diffusion coefficient . The results show that even 25% slag resulted in a substantial reduction in diffusion coefficient.

*Table 4. Strength and chloride diffusion properties of slag concretes (McGrath and Hooton 1997)*

| Property | Concrete A | Concrete B | Concrete C |
|---|---|---|---|
| % Slag | 0 | 25 | 40 |
| % Silica fume | 0 | 0 | 8 |
| W/CM | 0.4 | 0.4 | 0.3 |
| Strength (MPa) | | | |
| 7 day | 32.3 | 30.4 | - |
| 28 day | 39.1 | 41.2 | 65.9 |
| 56 day | 43.2 | 44.4 | 61.9 |
| Bulk Chloride Diffusion ($10^{-12}$ m$^2$/s) | 9.6 | 2.9 | 0.5 |

In Table 4, Concrete B is similar to normal bridge deck concrete used in bridge decks in Ontario. Concrete C with slag and silica fume is typical of high strength building columns in Toronto (Bickley et al 1991; 1994) and high performance precast tunnel elements (Hart et al. 1997) produced in Ontario. Slag improves these ternary mixtures by making the fresh silica fume concrete less sticky and easier to place and finish, while also providing for better long-term strength gain.

As stated earlier, the lower Ca/Si ratio and incorporation of alumina into the C-S-H resulting from slag will also increase chloride binding, helping to reduce the rate of chloride ingress. Thirdly, once the threshold chloride concentration to depassivate the steel has been reached, the increased resistivity of the pore system to OH- transport will reduce the rate of corrosion.

## 2.6. Carbonation-related corrosion

When $C0_2$ from the air reacts with cement paste, the $Ca(OH)_2$ carbonates to $CaC0_3$ and C-S-H breaks down into $CaC0_3$ and silica gel. This results in pH dropping to about 8 or 9, depassivating steel reinforcement. The best defence against carbonation is a dense, low permeability concrete and an adequate depth of cover (Parrott 1987). Because of the reduction of $Ca(OH)_2$ contents in slag concretes, concerns have been expressed about the potential for increased rates of carbonation. However, it was also found that for equal strength concretes with up to 50% slag, there is no detrimental effect on carbonation (Bier 1987). After 35 years of slag concrete use in Ontario, measured carbonation depths are very low and there have not been any cases of carbonation-related corrosion where proper depths of cover were maintained.

## 6.8. Freezing and thawing resistance

It is the North American experience that there is no detrimental effect of slag on resistance to freezing and thawing as long as the normal precautions are followed (Mather 1990):
(a) the coarse aggregate is not frost susceptible;
(b) the concrete has an adequate entrained air void system; and
(c) the concrete has achieved adequate strength before being exposed to freezing.

However, in laboratory tests, de-icer salt scaling resistance of slag concretes at high replacement levels (50% and higher) may be reduced (Afrani and Rogers 1994) but can be compensated for by higher (1-2%) air contents (Boyd and Hooton 2007). However, the Ontario Ministry of Transportation (MTO) currently limits the use of slag to 25% of cement, largely based on poor performance in ASTM C672 laboratory tests at higher replacement levels. Based on good performance observed by the author in several field trials in Ontario and in Quebec (Bouzoubaâ et al 2011), use of 50% slag may be of concern if good construction practices are not followed, but 35% should not (Boyd and Hooton 2007).

## 2.7. Alkali-silica reactivity

Slag has been found to be effective in controlling deleterious expansions from alkali-silica reactivity (ASR) when used in sufficient quantity (Duchesne and Berube 1994; Thomas and Innis, 1998). The Canadian Standard CSA A23.2-27A currently allows 35 -60% slag replacement for control of ASR depending on the reactivity of the aggregates, the length and type of exposure. Research indicates that lesser amounts can be effective with aggregates of slower reactivity. Thomas and Innis (1998) cast concrete prisms (CSA A23.2-l4A) with the Spratt reactive siliceous limestone and found that 50% slag was needed to keep 24- month expansions below the 0.040% limit in the CSA standard while the less reactive Sudbury greywacke containing gravel only required 35% slag replacement.

The slag helps reduce the hydroxyl ion content of the pore solution and incorporates higher level of alkalies (Na+ and K+) into its C-S-H matrix than does portland cement. This is shown in Figure 2 where concrete prism expansions (CSA A23.2-14A with reactive Spratt aggregate) are compared to pore solution alkalinity at 2 years for mixtures with slag, silica fume (SF) and slag-silica fume ternary binders (Bleszynski et al 2002). This data suggests that a suitable threshold to control expansion in concrete is 320-365 mM/L.

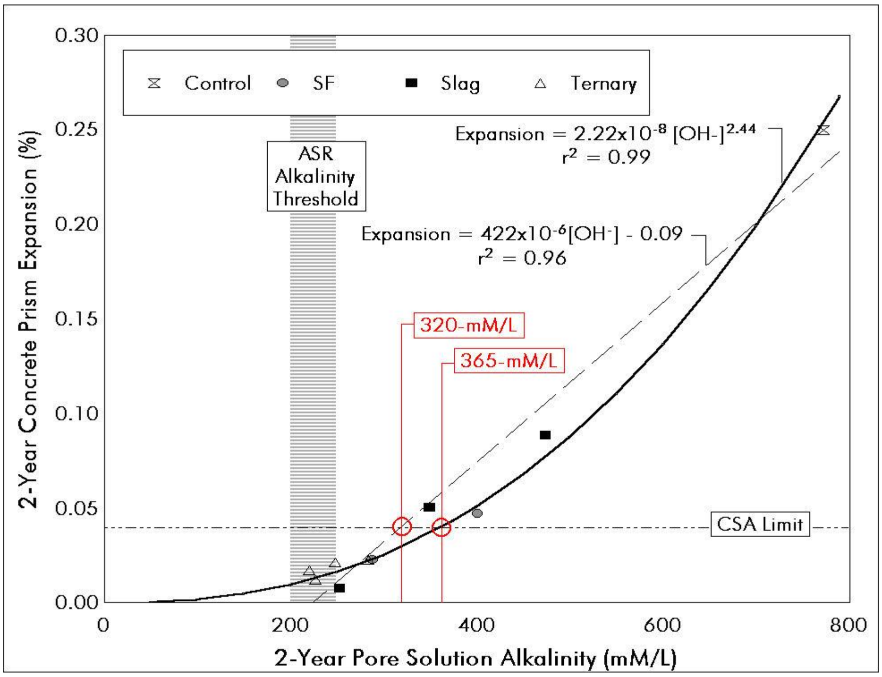

*Figure 2. Relationship between ASR concrete prism expansions and pore solution alkalinity (Bleszynski et al 2002)*

Several field exposure site trials have shown 50% slag to be effective in mitigating reactive aggregates after 20 years, as shown in Figure 3 (MacDonald et al, 2012, Bleszynski et al 2002)

In 1989, 50% granulated slag replacement was used to control a slowly expansive coarse aggregate (greywacke and microcrystalline quartz) in a series of concrete dams and powerhouses at the Magpie River Development in Ontario (Donnelly 1990). A field evaluation after 17 years found those structures to be uncracked, while a nearby portland cement highway bridge of similar age and made with the same cement and aggregates was map cracked and was found to contain ASR gel (Hooton et al. 2000).

A recent review on the use of slag and other SCMs to control AAR was produced by Thomas (2011).

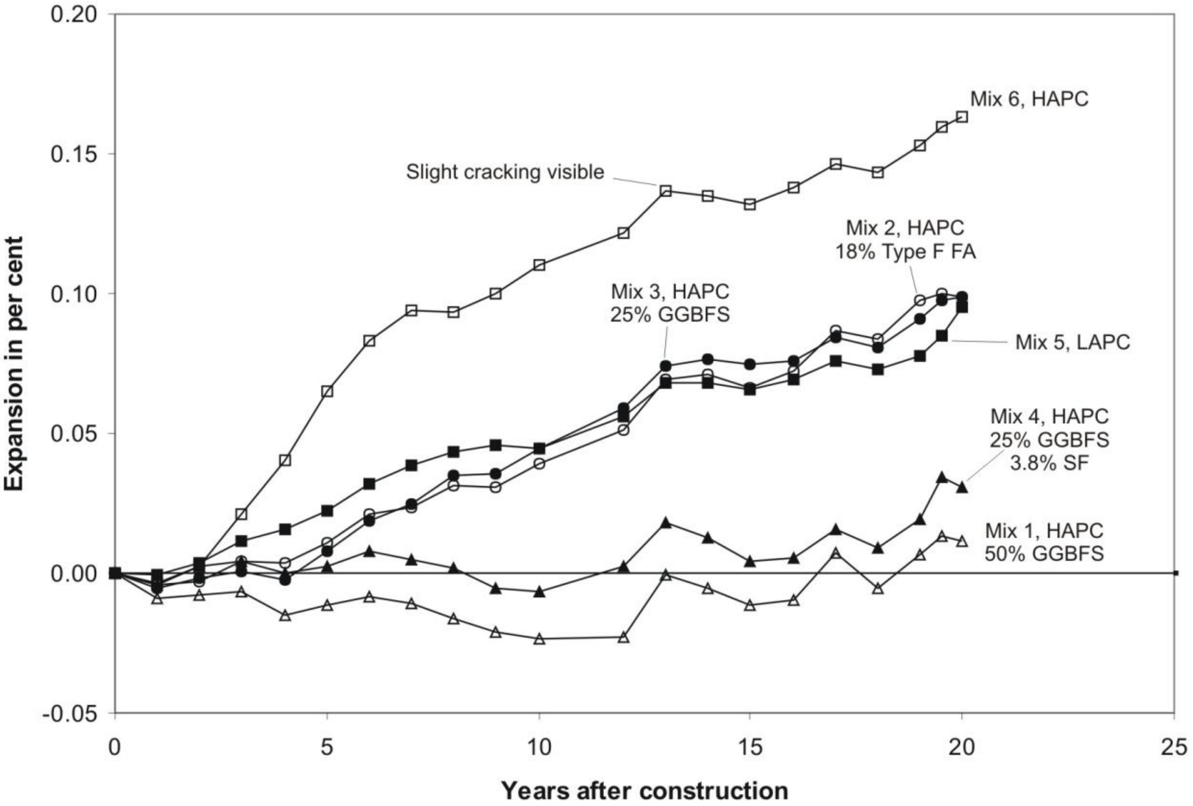

*Figure 3. Expansion of concrete pavement slabs made with reactive Spratt aggregate and different cementitious binders (MacDonald et al, 2012)*

## 3. USE OF SLAG IN TERNARY BLENDS

As mentioned previously, in Toronto numerous high strength buildings have been cast since 1986 using slag - silica fume ternary blends (Bickley et al, 1991; 1994). The advantage of slag in these ternary blends is to reduce stickiness by reducing required dosages of HRWR thus easing placement and finishing, reducing heat of hydration, and to maintain long-term strength gain. With use of accelerated curing, silica fume-slag ternary mixtures can develop high-early strength and maintain low chloride diffusion characteristics for use in precast operations (Titherington and Hooton 2004).

Segmental concrete tunnel liners for an extension of the Toronto subway requiring 100-year service life, segmental tunnel liner contract were cast using slag - silica fume mixtures achieving high strength and very low chloride diffusion levels of production units averaged only 0.5 x $10^{-12}$ $m^2/s$ (Hart et al. 1997). Similar concrete tunnel liners are being used in another new subway extension initiated in 2011. For high chloride penetration resistance, 40 road bridges at Toronto's Pearson airport were placed with slag - silica fume ternary mixtures between 1999 and 2004 and numerous high-performance highway bridge girders and decks were placed by the Ontario Ministry of Transport (MTO) since 1998. These bridge decks were 50 MPa, air-entrained concretes with ASTM C1202 coulomb values of < 1000 at 28 days.

As stated earlier, silica fume-slag ternary binders also work well to mitigate ASR (Bleszynski et al 2002; Hooton et al 2008; MacDonald et al 2012).

## 4. SUMMARY

Ground granulated blast-furnace slag, whether added separately to concrete or when used in a blended cement, can enhance durability, if concrete is properly proportioned and cured. It is effective in improving resistance to chlorides, sulphate, and alkali-silica reaction. Its use is typically only limited by availability and local economics.

In Ontario, separately ground slag has been in use for over 35 years and has been the predominant supplementary cementing material for over 30 years. Its use has been accepted for sulphate resistance, control of alkali-silica reaction, provision of low-heat, and for improved chloride penetration resistance, as well as being used in virtually all general purpose concrete applications.

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# NCF Workshops 1975 – 2012

*Thursday, 16 August 2012*

| No. | Date | Place and convenor | Theme | Documentation |
|---|---|---|---|---|
| **1** | 11.09<br>1975 | Dansk Betongforening København (P. Nepper-Christensen, A. Nielsen) | Termiske problemer ved udførelse av massive betongkonstruksjoner | Kompendium utgitt av Dansk Betonforening, november 1975. |
| **2** | 26.02<br>1976 | Avd. Betongbyggnad, Chalmers Tekniska Högskola, Gøteborg (A. Losberg) | Lettballastbetong som konstruksjons-materiale | Rapport 77:3 fra Institusjonen for konstruksjons-teknikk CTH, 1977. (Ikke anmäldt i Nordisk Betong). |
| **3** | 19.06<br>1976 | Cement- og Betonginstituttet, Stockholm (U. Bellander, G. Fagerlund) | Accelerade provningsmetoder | Majoriteten av rapporter publisert i Nordisk Betong, 5:1976. Øvrige rapporter (forfattere og titler) listet i samme nr. av Nordisk Betong). |
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| **5** | 09.06<br>1977 | Avd. för Byggnadsmateriallära Lunds Tekniska Høgskola. (L.O. Nilsson). | Fukt i betong | Anmält i Nordisk Betong 6:1977 av L.O. Nilsson |
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| **10** | Oktober 1979 | Det Norske Veritas (N. Ellingsvåg). | Utmattning av betongkonstruktioner | FCB-rapport. STF65 A80025, datert 80-06-10. |
| **11** | 16-17.10 1979 | Cement och Betonginstitutet, Stockholm (J. Byfors) | Betong och betongkonstruktioner i tidlig ålder | CBI-rapport finns. Kopia kan rekvireras från CBI. |
| **12** | 26.11 1979 | CBI, Stockholm (C. Molin) | Håltagning och rivning av betong | CBI-rapport finns ej och kommer ej heller att publiceras. |
| **13** | 21.03 1980 | DTH, København (K. Madsen) | Metoder och data för praktisk beräkning av svinn och krypning | Dialog Nordic Seminar on Deformations in Concrete Structures. Copenhagen March 1980, Nr 1-80 |
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| **28** | 05-05.02 1986 | Fortifikasjonförvaltningen, Stockholm | Dynamisk belastede betongkonstruktioner | Dynamisk belastede betongkonstruksjoner. Fortifikasjonsforvaltningen Forskningsbyraan. Rapport A4:86 Eskilstuna 1984 |
| **29** | 23.05 1986 | FCB/NTH, Trondheim | Utmatting av betongkonstruksjoner | Fatigue of Concrete. Papers presented at a Nordic mini-seminar Trondheim, 1985.SINTEF-rapport 5TF65 A86082 |
| **30** | 21.10 1986 | VTT Esbo | Betongkonstruksjoner under tvangsbelastning | Betongkonstruksjoner under tvangsbelastning. VTT-symposium 76 |
| **31** | 06.11 1986 | LTH Lund | Bruddmekanik | Fracture Mechanics of Concrete. Division of Building Materials, LTH, Lund November 6/86 |
| **32** | 20.11 1987 | Dansk Ingeniørforening, København | Hydrasjon av cement | Seminar om Hydration of Cement, Aalborg Portland, Februar 1988 |
| **33** | 18.02 1988 | VTT, Helsingfors | Bestandighet, livslengde | Durable concrete with industrial by-products. VTT Symposium 89. Esbo 1988 |
| **34** | 15.03 1988 | FCB, Trondheim | Fliskledt betong i våtrom – skader og utredning | Fliskledt betong i våtrom – skader og utbedring. SINTEF-rapport 5TF65 A88041, juni 1988 |
| **35** | 05.04 1988 | DTH, København | Kraftoverførsel til armering i revnet betong | Notits i Nordisk Betong 2:1988 |
| **36** | 15.11 1988 | FCB, Trondheim | Karbonatisering av betong | Karbonatisering av betong. SINTEF-rapport 5TF65 A88065 |
| **37** | 09.05 1989 | Dansk Ingeniørforening, korrosionscentralen | Kloridinitert korrosjon | Ingen publisering på dette miniseminaret. |

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| **38** | 02.06<br>1989 | FCB Trondheim | Betongkonstruksjoners brannmotstand | Fire Restance of Concrete. Papers presented at a mini-seminar Trondheim 1989 |
| **39** | 23-24.11<br>1989 | CTH Göteborg | Utmatting av betongkonstruksjoner | Fatigue of Concrete Structures.<br>CTH publikasjon P-90:8, Göteborg mai 1990 |
| **40** | febr.<br>1990 | Vegdirektoratet, Oslo | Høyfast betong i veier | - |
| **41** | 14.08<br>1990 | BML Trondheim | Fersk betongs reologi | - |
| **42** | 20.11<br>1990 | KTH Stockholm | Oforstorande provning av betongkonstruksjoner | - |
| **43** | 17.04<br>1991 | NTH/SINTEF, Trondheim<br>( Ø. Vennesland) | Elektrokjemiske metoder for rehabilitering av armerte betongkonstruksjoner | |
| **44** | 05.12<br>1991 | HTH, Oslo<br>(E. Sellevold) | Bindemidler i høyfast betong – reaktivitet, struktur og egenskaper | |
| **45** | 24.01<br>1992 | VTT, Esbo<br>(Juha Saarima) | Mikroskopi och Mildanalys | Microscopy and image analysis of building materials. Espoo, Finland, 1992. VTT Symposium 136, Technical Research Center of Finland, Espoo 1993, 54 pp ISBN 951-38 4087-5 |
| **46** | 19.11<br>1992 | Aalborg Universitetscenter<br>(L. Pilegaard Hansen) | Utmatting av betong | Fatigue of Concrete Structures. Dept. of Building Technology and Structural Engineering, Aalborg Universtetscenter, AUC, Aalbort 1992, 126 pp, ISSN 0902-7513-R9307 |

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| **47** | 13-14.01 1993 | CTH, Göteborg (L.O. Nilsson) | Kloridtransport i betong | Cloride penetration into concrete structures. Institutionen för byggnadsmaterial, Chalmers Tekniska Högskola, Publication 93:1, Göteborg, Januari 1993 |
| **48** | 22-23.04 1993 | Lund University (Göran Fagerlund, Erik J. Sellevold) | Nordisk Miniseminar NBS-MK Frost | Mødereferat |
| **49** | Juni 1995 | Aalborg | Modern Design of Concrete Structures | |
| **50** | 16-17.04 1996 | Lund University (Sture Lindmark, Göran Fagerlund) | Frost Resistance of Building Materials | Report TVBM-3072 |
| **51** | 08.11 1996 | Tekniska Högskolan i Luleå (Hans Hedlund, Patrick Groth) | Licentiatseminarier | |
| **52** | 28.11 1996 | NTNU/SINTEF, Trondheim (E. Sellevold, T.E. Hammer) | Early volume change and reactions in paste – mortar – concrete | |
| **53** | 10.12 1996 | CBI Stockholm | Livslängdbedömning inkluderande korrosionens propageringsskede | |
| **54** | 10.07 1997 | Lund University (Göran Fagerlund, Bertil Persson) | Self Desiccation of Concrete | Report TVBM-3075 |
| **55** | 22.08 1997 | VTT, Esbo | Fuktmätning och fukttransport i betongkontstruktioner utsatta för temperatur- och fuktvariationer | VTT Symposium No 174 ”Moisture Measurements” |
| **56** | 18.06 1999 | Lund University (Göran Fagerlund, Bertil Persson) | Self Desiccation of Concrete | Report TVBM-3085 |
| **57** | 31/08+1/0 91999 | Lund University ( Katja Fridh, Göran Fagerlund) | Frost Resistance of Building Materials | Report TVBM-3087 |
| **58** | 07-08.10 1999 | Skagen (Dirch H. Bager) | Water in Cement Paste & Concrete – Hydration and Pore Structure | Workshop Proceeding No.1, Nordic Concrete Federation 1999 |

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| **59** | 01.09<br>2000 | DTU / Lyngby<br>(Mette Geiker,<br>Henrik Stang) | Steel Fibre Reinforced Self-Compacting Concrete | |
| **60** | 26-27/4<br>2001 | Trondheim<br>(Kåre Johansen) | Self Compacting Concrete | SINTEF Report STF22 A01614 |
| **61** | 22-23/05<br>2001 | Chalmers<br>(L.O. Nilsson) | Armeringskorrosion och chlorider i betong | |
| **62** | 12-13/06<br>2001 | KTH / Stockholm<br>(Johan Silfwerbrand) | Fibre-reinforced Concrete Structures | Workshop Proceeding No.2, Nordic Concrete Federation 2001 |
| **63** | 21-23/11<br>2001 | Hirtshals<br>(Dirch H. Bager) | Durability of exposed Concrete containing Secondary Cementitious Materials | Workshop Proceeding No.3, Nordic Concrete Federation 2001 |
| **64** | 14-15/6<br>2002 | Lund University<br>(Göran Fagerlund,<br>Bertil Persson) | Self Desiccation of Concrete | Report TVBM-3104 |
| **65** | 29/8<br>2002 | CBI<br>(Johan Silfwerbrand) | Diagnos av bärande konstruktioner | CBI rapport |
| **66** | 22-23/5<br>2003 | Teknologisk Institut<br>(Claus V. Nielsen) | Concrete and Fire | Summary paper in NCR 2:03 |
| **67** | 6/10<br>2003 | Veidekke ASA/Oslo<br>(Terje Kanstad) | Design Rules for Steel Fibre Reinforced Concrete Structures | Workshop Proceeding No.4, Nordic Concrete Federation 2003 |
| **68** | 3-4/11<br>2003 | Teknologisk Institut<br>(Lars Nyholm Thrane) | Form Filling Ability of Self-compacting Concrete | Summary paper in NCR 2:04 |
| **69** | 31/3+1/4<br>2005 | NTNU / Trondheim<br>(T. Kanstad,<br>Ø. Bjøntegaard,<br>E.J. Sellevold) | Crack Risk Assessment of Hardening Concrete Structures | Workshop Proceeding No.5, Nordic Concrete Federation 2005 |
| **70** | 25-26/10<br>2007 | Helsinki<br>(Stefan Jacobsen/NTNU & AkerArktic) | Ice Abrasion on Concrete Structures | Workshop Proceeding No.6, Nordic Concrete Federation 2008 |
| **71** | 15/11<br>2007 | NTNU / Trondheim<br>(Terje Kanstad) | Fibre Reinforced Concrete | Workshop Proceeding No.7, Nordic Concrete Federation 2008 |
| **72** | 12-14/11<br>2008 | Hirtshals<br>(Eigil V. Sørensen) | Nordic Exposure Sites - Input to revision of EN 206-1 | Workshop Proceeding No.8, Nordic Concrete Federation 2008 |
| **73** | 2-5/3<br>2010 | Vedbæk<br>(Dirch H. Bager) | Freeze-thaw Testing of Concrete -<br>Input to revision of CEN test methods | Workshop Proceeding No.9, Nordic Concrete Federation 2010 |

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| **74** | 13/10 2011 | Chalmers / Gothenburg (Karin Lundgren, Mikael Hallgren) | Finite Element Analysis of Concrete Structures | Summary paper in NCR, December 2012 |
| **75** | 15-16/2 2012 | Oslo<br>(Bård Pedersen, Claus K. Larsen & Dirch H. Bager) | Durability aspects of fly ash and slag in concrete | Workshop Proceeding No. 10, Nordic Concrete Federation 2012 |

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