SINTEF Building and Infrastructure Jan Lindgård (main author and editor)

RILEM TC 219-ACS-P: Literature survey on performance testing

COIN Project report 27 - 2011

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FA 3.2 Service Life

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A through arch bridge crossing Iddefjord at Svinesund, and joining Sweden and Norway.

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Preface

RILEM TC-219 ACS “Alkali aggregate reactions in Concrete Structures” (2007-2012) is mandated with an almost total review and issuing of assessment and testing procedures regarding alkali aggregate reactions in concrete, as well as the application of these procedures.

One of the TC task groups is tasked with the preparation of a testing procedure for performance testing of concrete, enabling the correct assessment of concrete constituents and their combinations, i.e. concrete mix design. The present report forms the compilation and discussion of the theoretical basis for the set-up of a performance test method and its application.

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The present report to a large extent results from voluntary and un-paid work, and we greatly appreciate the contributions from the authors that have had the main responsibility for the various sub-chapters and the corresponding appendices – see Appendix 1. The authors are listed in alphabetical order:

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Preface (COIN)

The present work is issued within the framework of the COIN centre:

COIN - Concrete Innovation Centre – is one of currently 14 Centres for Research based Innovation (CRI), which is an initiative by the Research Council of Norway. The main objective for the CRIs is to enhance the capability of the business sector to innovate by focusing on long-term research based on forging close alliances between research-intensive enterprises and prominent research groups.

The vision of COIN is creation of more attractive concrete buildings and constructions. Attractiveness implies aesthetics, functionality, sustainability, energy efficiency, indoor climate, industrialized construction, improved work environment, and cost efficiency during the whole service life. The primary goal is to fulfil this vision by bringing the development a major leap forward by more fundamental understanding of the mechanisms in order to develop advanced materials, efficient construction techniques and new design concepts combined with more environmentally friendly material production.

The corporate partners are leading multinational companies in the cement and building industry and the aim of COIN is to increase their value creation and strengthen their research activities in Norway. Our overall ambition is to establish COIN as the display window for concrete innovation in Europe.

About 25 researchers from SINTEF (host), the Norwegian University of Science and Technology - NTNU (research partner) and industry partners, 15 - 20 PhD-students, 5 - 10 MSc-students every year and a number of international guest researchers, work on presently 5 projects:

- Advanced cementing materials and admixtures
- Improved construction techniques
- Innovative construction concepts
- Operational service life design
- Energy efficiency and comfort of concrete structures

COIN has presently a budget of NOK 200 mill over 8 years (from 2007), and is financed by the Research Council of Norway (approximately 40%), industrial partners (approx 45%) and by SINTEF Building and Infrastructure and NTNU (in all approx 15%).

For more information, see www.coinweb.no

Tor Arne Hammer
Centre Manager

Summary

Assessment of influencing parameters

The comprehensive literature survey has been a joint work within the task group "Performance testing" in RILEM TC 219-ACS. 12 authors have contributed to a various extent. In total, about 250 titles are included in the report reference list. Even more references are included in the various appendices. Our opinion is that all the main parameters of significance for alkali-silica reaction (ASR) performance testing are included in the assessment. Alkali-carbonate reaction (ACR) has not been focused on in this literature survey.

The main focus in the literature survey has been to assess how various parameters may influence the laboratory/field correlation with respect to ASR performance testing, either directly or indirectly.

Parameters of high importance

The review revealed that the following ASR related parameters are of high importance for the outcome of a laboratory performance test, and thus on the laboratory/field correlation:

- Properties of hydration products
- Internal relative humidity
- Temperature
- Aggregate reactivity
- pH of the concrete pore solution
- Properties of reaction products
- Air-content

The report discusses how various *laboratory exposure conditions, aggregates types, binder types, mix designs* and *casting procedures* may influence these parameters.

Need for further research

Based on the literature survey and on discussions in the task group "Performance testing" in RILEM TC 219-ACS, issues that need further research are divided into:

- Parameters critical for drafting a performance test procedure set-up
- General parameters, but not critical for the work in the "performance group"

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1 Introduction

1.1 Background

National regulations for preventing alkali-silica reaction (ASR) in concrete structures are based on various principles that have to take into account a range of material properties and local experience. In order to improve flexibility, extend material selection criteria and optimize concrete mix design, some countries have incorporated the option of performance testing in their provisions. Such options are meant to partly replace strict and technically-commercially restraints by a performance-oriented requirements concept – or to set the details for concrete mix design based on local material expertise and experience.

Performance testing implies by definition some kind of acceleration of the deleterious reaction occurring naturally under ambient conditions. Submitting concrete to accelerated testing by nature changes the kinetics, thermodynamics and boundary conditions, to which its constituents are exposed.

In order to maintain the relevance to field structures when testing in the laboratory, it is crucial that the basic conditions do not change to an extent where the correlation of performance ranking under the two different conditions does not anymore exist. Hence, performance testing in the present context is not about predicting an exact level of deterioration with the selected materials and design, but to determine a relative level of performance with the perception that test results conforming to certain acceptance criteria will assure acceptable field performance.

This field versus laboratory performance correlation can basically be established by establishing a comprehensive set of data from the two conditions or by ensuring 100% field-related laboratory conditions. None of these approaches are feasible: Setting up a performance test will require both theoretical considerations and practical verification. The present report attempts to review parameters from a theoretical point of view, limiting the testing procedural degree of freedom – and possibly that of the material selection to be submitted for testing.

The objective of the present report is to display parameters and limitations in view of accelerating ASR under moist and elevated temperature conditions. These concerns will be taken into account for developing an ASR performance test, whereby identified challenges should be dealt with in one of the following ways:

- Research needs to be followed up for initiation, reporting and results implementation (i.e. the performance test not to cover the specific issue until further research has been accomplished).
- Experience based convention for agreed, unified approach
- Phenomenon discussed can be dealt with within level of chosen safety margin
- Scatter introduced by the specific or collective phenomenon(s) of concern can be determined by a precision test

1.2 Technical background - challenges

To be able to utilize alkali-silica reactive aggregates for production of durable concretes, there is a need for a reliable performance test to evaluate the alkali reactivity of concrete mixes and/or binders resistant to alkali-silica reactions. Several such performance tests have been used worldwide for at least 15 years, mainly to evaluate supplementary cementing materials (SCMs) and lithium as means for avoiding damaging ASR in concrete. In principle two groups of accelerated laboratory performance test methods exist, one using mortar bars and the other using concrete prisms. However, the test conditions (e.g. temperature) used within these two groups might vary widely from one test method to another. Thus, the results/conclusions from different test methods may vary.

Thomas et al. (2006) have recently provided a critical evaluation of different test methods. The authors concluded that none of the currently available or commonly used test methods meet all the criteria for an ideal performance test. For example, the main shortcoming of the Canadian 38°C concrete prism test (CPT) (Canadian Standards Association, 2000) is the duration of the test (2 years) and that the addition of alkalis is required to compensate for alkali leaching effects (i.e. the fact that alkalis are leached out of the prisms during exposure in the humid environment). Thus, they claim that the method cannot be used to determine the "critical" alkali content for an alkali reactive aggregate, nor determine how the minimum level of a SCM changes with the concrete alkali content. However, research is going on towards improving current test methods and developing alternative tests, for instance within our RILEM technical committee TC 219-ACS. Similar work has also been started in USA by the U.S. Department of Transportation (Allen and Brumfield, 2006).

Main challenges

Development of accurate and reliable performance tests for production of durable concretes is a challenge. Several requirements must be fulfilled, some being somewhat contradictory. On the one hand the test methods should be inexpensive and rapid, calling for extremely accelerated test conditions. On the other hand a performance test should mirror the field performance of the actual concrete for up to a 100 years lifetime. Another important requirement is the possibility to test job mixes with identical aggregate and concrete composition that will be used on actual projects. Use of mortar bars is in conflict with this latter requirement.

According to Thomas et al. (2006) other important requirements for an ideal performance test for ASR are:

- The test should be capable of evaluating the "critical" alkali contents, i.e. the alkali leaching problem must be solved to avoid the need for a boosted alkali level
- The test should be capable of assessing all types of SCMs, lithium compounds and combinations of SCM and lithium, with cements of different alkali level

Crucial parameters to ensure a good laboratory/field correlation

As stated by Thomas et al. (2006) the only suitable benchmarking of a laboratory performance test is against real concrete structures (if available) or as a surrogate against large concrete blocks exposed outdoor. However, such long-term field experience is lacking for most commercial SCMs. When developing an accelerated performance test, it is thus crucial to evaluate fundamental questions in order to ensure a satisfactory laboratory/field correlation. Three main questions are:

1. Does the test ensure a sufficient high moisture level within the test specimens? (regardless of binder composition and water / binder ratio?)
2. Are the alkalis kept inside the test specimens during the test period? (i.e. is there significant alkali leaching during the exposure period?)
3. What is the effect of elevating the temperature? (i.e. how to accelerate the ASR without changing the reaction mechanisms, e.g. the solubility of silica or the type of hydration products formed during hydration?)

Consequently, the main focus needs to be put on the three fundamental parameters assumed to have the primary influence on the outcome of an accelerated laboratory performance test. These are:

- Humidity
- Alkali content ("controls" the concentration of OH^- in the pore solution)
- Temperature

However, also other parameters may influence the laboratory/field correlation, either directly or indirectly, for instance by affecting the humidity or the alkali content of the test samples. This is further discussed in the current report.

1.3 Assessment of influencing parameters

The main focus in the literature survey has been to assess how various parameters may influence the laboratory/field correlation with respect to ASR performance testing, either directly or indirectly. More exactly is the aim to evaluate how various *laboratory exposure conditions, aggregates types, binder types, mix designs* and *casting procedures* may influence the following important ASR related parameters;

- *Internal humidity* of the concrete prisms
- *Composition of the concrete pore solution* during testing (keywords; alkali leaching, alkali release from aggregates, influence of $Ca(OH)_2$, alkali content, concentration of OH^-)
- *Properties of hydration products formed* during hydration / exposure
- *Aggregate reactivity*
- *Type and properties of reaction products formed* during exposure (i.e. primarily ASR-gel, but also any ettringite or delayed ettringite formation (DEF))

An overview of the influencing parameters discussed, including a list of authors that have had the main responsibility for the various topics, is given in Appendix 1. To get an overview of the most important parameters to take into account, most authors have given each parameter an influencing number" (0, 1, 2 or 3, respectively). These numbers are not included in the report, but have been used by the task group during the preparation of the report.

2 Internal humidity

For details, see Appendix 2A, 2B and 2C.

2.1 Mechanisms

2.1.1 Moisture content

Description of the moisture conditions in concrete
The moisture condition in concrete can be described in two different ways:

1. The thermodynamic state of the pore water, typically expressed as relative humidity (RH) at a certain temperature.
2. The pore water content determined by drying and weighing. May be expressed either as the percentage of mass or volume, or as the degree of saturation.

It is important to note that the relative humidity is a measure of the thermodynamic state of the pore water, and is not a direct measure of the amount of water. At a given moisture content, the RH is a function of the pore structure, the temperature, the chemical composition of the pore water and the moisture history of the concrete.

The role of water in the Alkali-Silica Reaction
Moisture is generally accepted to be one of the main factors affecting ASR. Water is important as a transport media for ions. The role of water is even more important in the expansion stage. The overall expansion and cracking of concrete is basically due to sorption of water by the alkali-silica gel, which in turn swells and thereby causes damage.

The water content in ASR-affected structures is normally expressed as RH. However, the measurement of RH is notoriously very difficult and uncertain, particularly in the field. The degree of capillary saturation (DCS) may be a more suitable parameter to characterize the water content and the progress of damage on structures due to ASR. The relation between RH and DCS for different concretes, which is described by adsorption or desorption isotherms, varies depending on several factors, where the water-to-cementing-materials[1] (w/cm) ratio = water/binder (w/b) ratio is the most important one, see Figure 1.

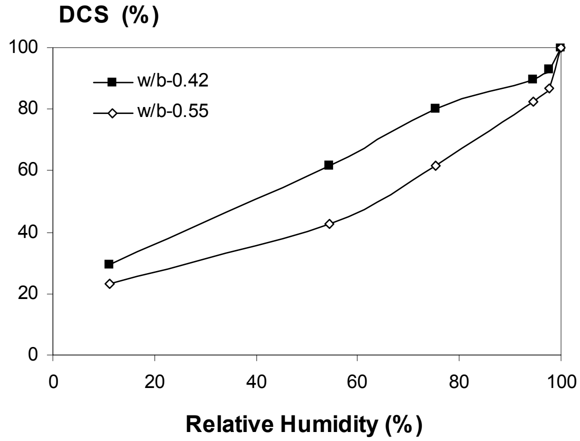

Figure 1. Desorption isotherms for concrete discs by the degree of capillary saturation (DCS) as a function of RH for two laboratory concretes of different w/cm ratio (the concrete with w/b ratio = 0.42 contained 5% silica fume) (Relling, 1999).

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[1] Further in the report, w/cm and w/b are used interchangeably, while w/c is used if only OPC.

The critical limit for developing ASR is reported to lie in the range 80-90% RH depending on several factors, as discussed by Larive et al. (2000). With only a few exceptions, Lindgård et al. (2006) found that DCS of Norwegian concretes with pronounced ASR was higher than 90%.

Literature survey
The questions, hypotheses and statements in Appendix 2A and the chapters 2.2-2.5 are given under the supposition that the laboratory testing must secure a high internal humidity within the concrete. This means that the internal moisture content is aimed to be higher than in most real concrete structures, i.e. the tested concrete recipes and binder types are given “worst-case humidity conditions” in the laboratory testing.

2.1.2 Self-desiccation (RH)

Mechanisms causing self-desiccation
The hydration process of the cement gives a reduction of the volume. This is due to the fact that the reaction products (i.e. C-S-H gel and CH) have a smaller volume than the reactants (cement + water). This phenomenon is referred to as chemical shrinkage, and has some major effects:

1) It causes autogenous shrinkage, which is a volume contraction of the total concrete body. In the plastic phase, the chemical shrinkage equals the autogenous shrinkage.
2) In the hardening phase, the chemical shrinkage results in empty pores within the concrete. These pores will remain empty if no water is supplied from the surroundings. This leads to a lowering of the RH in the concrete, a phenomenon called self-desiccation. At low w/c ratios (<0.40) this effect is large and may reduce the RH below 80% beyond a period of time.
3) When water is gradually consumed during the hydration process and the chemical shrinkage pores are left empty, the remaining water will be in a state of “tension stress”. This is the mechanism explaining the autogenous shrinkage in the hardening state.

In Appendix 2B and the chapters 2.2-2.5, the effects of self-desiccation on the RH are discussed. The direct effects of autogenous shrinkage, i.e. any external volume changes, are treated in Appendix 2C, together with the effects of drying shrinkage.

2.1.3 Shrinkage

Mechanisms of volume changes
A number of different mechanisms may lead to volume changes of concrete, both in the plastic phase and in the hardening phase. Relevant mechanisms for the hardening phase, which are discussed in Appendix 2C and in the chapters 2.2-2.5, are:

- Autogenous shrinkage (see also Appendix 2B)
- Drying shrinkage
- Temperature movements

The magnitude of shrinkage may be relatively high compared to the measured length increase caused by ASR. A couple of examples:

- Self-desiccation shrinkage of a concrete with w/b 0.35 may be in the order of 0.01% after one week curing (Bjøntegaard, 2001).
- Long-term drying shrinkage in dry conditions (RH of 50%) may be higher than 0.1%, as stated by Sellevold (1992) and Neville (1995).
- Long term drying shrinkage may be in the order of 0.04% when stored in 80% RH (Neville, 1995).

2.2 Influence of storage conditions

2.2.1 Moisture content

The micro climate in a storage container is of great importance for the internal humidity of the concrete prisms. It is essential to obtain a homogenous and high RH in the whole container. Important parameters are size and design of storage containers, type of lining (if any) and application of a watertight sealing. Too large containers may lead to an in-homogeneous distribution of moisture. For example, the experience gained with the Norwegian 38°C CPT (Norwegian Concrete Association, 2005) when large storage containers holding several concrete prisms were replaced by smaller containers holding only 3 prisms in each, was a general increase in expansion. With the introduction of the smaller containers, also the Norwegian sandstone, proven to be reactive in field, showed expansions above the critical limit (Wigum and Lindgård, 2008).

The susceptibility to loss of moisture during the exposure period will increase with increasing storage temperature. The extent of any weight loss is controlled by the relative humidity in the surroundings and the type of container. If concrete prisms are stored over water in containers placed in a dry and hot room, as the case is for several concrete prism tests (Norwegian Concrete Association, 2005; Canadian Standards Association, 2004; RILEM, 2000), the risk of drying is high compared to storage in containers placed in a humid environment - e.g. in a reactor, as in the RILEM AAR-4.1 CPT (RILEM, 2006). If the lid is broken or eventually not sufficiently made watertight, the risk of evaporating the water in the bottom of the container is significant. Also the storage time influences the sensitivity to loss of water. For instance, SINTEF have experienced that RILEM AAR-3 containers (RILEM, 2000) are particularly vulnerable to drying due to the small amount of water in the bottom of the containers (only 350 ml) combined with a long testing time (one year). As several have reported, e.g. Lindgård et al. (2008), normally the weight of the prisms increases with expansion and with time, after a possible weight loss in the first weeks. However, if the prisms show weight loss over time, this must be due to insufficient water in the system and a too low expansion will be recorded.

Submerged storage of the prisms will give rise to high internal water content, unless large test specimens and a low w/c ratio are applied (see 2.5.1). One consequence of the likely higher moisture content in submerged concrete prisms, compared to most field concrete structures, is development of a less swelling gel due to a reduced viscosity (see 7.1). Another important consequence of submerging in water, also leading to reduced expansion, is enhanced leaching of alkalis (see 3.2).

Wrapping of concrete prisms, by use of moist cotton cloths and plastic sheets, are applied in some test methods either with aim to secure a high moisture content surrounding the prisms or to reduce the extent of leaching of alkalis. The wrapping may, however, reduce the access to ambient moisture in the air. If the wrapping effectively hinders contact between the ambient moisture content in the storage container and the prisms (e.g. as in the RILEM AAR-3 CPT (RILEM, 2000), where the wrapped prisms are stored in plastic bags), the amount of water added during the wrapping procedure and on top of the prisms at every measuring point of time may have high influence on the internal moisture content within the concrete prisms.

The curing temperature may influence the concrete porosity and permeability. A higher curing temperature will normally lead to a coarser porosity and consequently an increased permeability, as reported by Kjellsen et al. (1990; 1992) and Lothenbach et al. (2007). As a consequence, the applied curing and storage temperature may influence water uptake, water transport and drying properties, and thus also the internal moisture content during accelerated laboratory testing.

With the use of supplementary cementing materials, SCMs, the effect of increased temperature on the properties of the concrete is believed to be higher. In particular, the temperature may influence the properties of hydration products formed during hydration and the rate and extent of hydration (see 4.1). If SCMs are applied as a tool to combat ASR, an early elevated temperature may thus influence the outcome of an accelerated performance test. An important question, discussed by Bokern (2008), is whether elevated temperature accelerates the pozzolanic reaction more than the ASR. If so, the outcome of the laboratory test may be too positive compared to expected long time field behaviour. As a consequence, Bokern recommends allowing the concrete to hydrate sufficiently, e.g. 28 days at 20°C, before starting the ASR testing - see also further discussion in chapter 3.4 (Schmidt et al., 2009). A prolonged curing time will, however, also favour the pozzolanic reaction. In addition, it may reduce the concrete internal humidity due to higher extent of self-desiccation. If rather large concrete prisms and a low w/b ratio are applied, the combination of high degree of self-desiccation and a dense, well cured concrete may lead to a permanent lowered internal RH in the prisms (see later).

Starting a performance test one day after casting is not recommended at FIB (Bauhaus-University Weimar, Department of Civil Engineering, F.A. Finger-Institute for Building Materials Science). At this stage, the microstructure (hydration degree, pore size distribution) of the paste is not the same as in the field, where concretes are usually cured for at least some days. Before testing various concretes in their cyclic climate chamber, where normally different de-icing salts are added, they pre-store the concretes at 20°C for 7 days (OPC concretes) or at least 28 days (SCM containing concretes) – see also chapter 3.5 and 4.1.

The sorption properties and the internal RH in concrete are to a certain degree dependant on the storage temperature. A raised temperature in a part of a concrete sample /structure will lead to increased local vapour pressure. This will initiate moisture transport from warmer to colder regions and, eventually, reduce the local moisture content, and as a consequence lead to a decrease in RH, as discussed by Nilsson (2006). This phenomenon will take place during cooling of concrete prisms overnight, before the prisms are measured the day after. During cooling, moisture will move from the warmer inner part to the colder outer parts. If the prism are wrapped, e.g. as in the RILEM AAR-3 method (RILEM, 2000), the extent of evaporation during cooling and measuring will be reduced (Lindgård, 2009).

On the other hand, if the moisture content within a concrete is rather constant (as one can assume for small concrete prisms stored over water in a sealed container, at least if the w/c ratio is not too low), a general increase in the temperature will give rise to a small increase in the internal RH. For example, according to tests reported by Sjöberg et al. (2002), the RH within a concrete with w/c 0.40 and internal RH 90% will increase approximately 0.25% per °C. Thus, an increase of the concrete temperature from 20°C to 40°C may increase the internal RH with approximately 5%. The effect decreases with increasing internal RH and with increasing w/c ratio (Sjöberg et al., 2002; Nilsson, 2006). One consequence of this phenomenon is that the internal RH in concrete prisms will increase with increasing storage temperature, provided no change in the concrete internal moisture content.

If the size of concrete specimens increases, the probability for development of a moisture profile through the cross-section will increase. In particular this is the case for large concrete field cubes and massive concrete structures, but this may also occur in concrete prisms with rather large cross-sections (e.g. 100 x 100 mm^2). Several authors, e.g. Stark (1991) and Sellevold (1993), have shown that moisture fluctuations in the field basically take place in the outer layer (some cm's) of the concrete. The depth of the influenced zone will decrease with decreasing w/c, as shown by Yang et al. (2005), due to a reduced permeability. As a consequence, the residual concrete mix water, depending on the w/cm ratio, rather than ambient wetting and drying determines the prevailing moisture content in the interior of massive concrete structures, as discussed by Stark (1995). For such structures the extent of self-desiccation, mainly controlled by the w/cm ratio, may govern the interior RH level of the concrete (see 2.5.1 and 2.5.2).

2.2.2 Self-desiccation (RH)

The major parameter with respect to lowering of RH due to self-desiccation is mix design of concrete, where w/cm ratio is the single most important parameter. Generally, the effect increases with decreasing w/cm. For practical purposes the effects of self-desiccation becomes important for concretes with w/cm ≤ 0.45.

Also conditions during curing and exposure may have some influence on the degree of self-desiccation. Elevated temperature in the early hardening phase will increase the hydration rate, which will lead to self-desiccation at an earlier point of time. This may lower the resulting RH if the self-desiccation pores are not allowed to be filled during the curing/exposure period. A consequence could be a reduction, or at least a time delay, in the resulting expansions due to ASR.

Submerging will counteract, and in most cases likely totally hinder, a reduction of the RH due to self-desiccation. However, Nilsson (2002) has shown that submerged high performance concrete (w/b approximately 0.30) may not be saturated due to self-desiccation and extremely slow moisture transport into the concrete. In particular, a combination of thick specimens and low w/c will hinder pore filling by water (see further discussion on prism size below).

When “water tight” wrapping is applied, the resulting RH in the concrete may be more or less controlled by self-desiccation if there is limited access to external water. For such a situation, the initial curing time and curing conditions becomes more important to secure high RH during the exposure period.

Increasing prism size will generally increase the influence of self-desiccation on the resulting RH. In general, at depths > 50 mm from the surface layer of the concrete, the RH is basically controlled by self-desiccation and to a very low degree by the surroundings of the concrete body (Stark, 1991). This is very important to bear in mind when designing large concrete specimen for outdoor exposure experiments. The larger the specimens get, the more will the internal RH be a result of the w/c instead of the moisture conditions of the surrounding.

2.2.3 Shrinkage

The temperature during curing, storage and measurement is relevant with respect to shrinkage / volume stability. Increased curing temperature will accelerate the hydration rate and may lead to increased shrinkage during the first days and weeks of curing. This is relevant for the reference length measurement (i.e. the initial length readings).

Whether the prisms are cooled or not prior to measurement may also be of significance. If the prisms are cooled before they are measured, this may lead to loss of moisture (moisture will move from the warmer inner part to the colder outer parts) leading to shrinkage. This effect will be less for wrapped prisms due to lower weight loss during cooling (see also 2.2.1).

Another important factor is to keep the internal prism temperature constant during all measurements. Several methods state that the maximum allowed variation in the room temperature where the prisms are being stored before and during the measurements is ±2°C, e.g. RILEM AAR-3 (RILEM, 2000) and the Norwegian CPT (Norwegian Concrete Association, 2005). But how sensitive is the measured expansion to a moderately deviating prism temperature at measuring compared to the temperature during the reference measurement? A concrete will expand approximately 0.001% if the temperature increases 1°C (Aalborg Portland, 1979). This means that a 5°C temperature change corresponds to approximately 0.005% length change. When the critical expansion limit for several concrete prism methods is in the range 0.030-0.040%, a 5°C temperature change constitutes 1/6 to 1/8 of the critical expansion limit.

An aspect that significantly can influence the reference length of the prisms (being the basis for calculating the expansion), is whether the initial length readings are taken immediately after de-moulding or after a 30 minutes submerging in water, e.g. as in the RILEM AAR-4.1 60°C CPT (RILEM, 2006). Without submerging, the internal prism temperature may be somewhat higher than 20°C due to the cement hydration. If submerged, the water temperature will control the internal prism temperature. If the quality control in some laboratories is not satisfactory, a temperature variation up to 5°C is likely to occur.

The extent of shrinkage depends on the loss of moisture due to drying – and the reduction in RH due to self-desiccation. The moisture conditions during exposure influences the total shrinkage. While dry conditions during storage may cause a resulting shrinkage, submerging, on the other hand, will cause swelling of the specimens (Neville, 1995). Another important thing to bear in mind is that one part of the total shrinkage is reversible while one part is irreversible.

For the cyclic climate storage at FIB, initial readings are taken after the very first drying phase in order to cancel out the shrinkage of the prisms. It turned out to be important to consider the different shrinkage behaviour of different concretes and to “normalize” the zero-readings. The expansion after the following very first wetting and freeze-thaw-cycling phase is typically around 0.2 mm/m (‰) and is caused by water absorption. Only expansion beyond this hygric expansion (> 0.2 mm/m = ‰) is attributed to other and possibly deleterious mechanisms (Giebson et al., 2010a). The readings are always taken after the prisms have reached a core temperature of 20°C. A deviation of ± 2 °C is allowed and has, based on own experiences, no significant effect on the measurements.

One important question has to be asked: *What is the most correct “reference length” to apply in ASR testing; the length after de-moulding, the shortest length after some shrinkage has occurred or the length after a pre-curing period?* The magnitude of the irreversible shrinkage will also influence this question.

2.3 Influence of aggregate type

2.3.1 Moisture content

The aggregate water absorption may influence the internal moisture content in the concrete, in particular for concretes with a low w/c ratio. A highly porous aggregate may supply the paste with a considerable amount of moisture during the curing and subsequent exposure, and thus counteract the internal drying due to self-desiccation. It is possible that the addition of wet lightweight aggregate particles can be used as a means to reduce the autogenous shrinkage caused by self-desiccation, as shown by Hammer et al. (2004) and Lura et al. (2007). Theoretically only 15 l/m^3 of extra water is needed to fill the empty pore space generated by cement hydration (self-desiccation pores) of a concrete with w/c

0.40, 400 kg/m^3 cement and 65% degree of hydration (Hammer et al., 2004). As a consequence, the extent of water absorption and the degree of saturation of normal weight aggregates may influence the internal RH in a concrete. As Hammer et al. (2004) concluded, a saturated aggregate with 0.8% water absorption may theoretically supply a "w/c 0.40 concrete" with sufficient moisture to totally counteract the drying due to self-desiccation (see 2.5.1).

2.3.2 Self-desiccation (RH)

The aggregate water absorption may be of relevance as a water supply, as discussed in 2.3.1. The water supply from aggregate pores may then counteract the self-desiccation effect on RH.

2.3.3 Shrinkage

Porous aggregates with high water absorption may act as a water supply and counteract shrinkage (see also 2.3.1). This has recently been shown by Meddah & Sato (2010). In that particular study, highly porous ceramic aggregate (absorption of 9.3%) was used. The relevance for "normal" aggregates with absorption around 1% needs to be further investigated.

According to Neville (1995), the following issues with respect to aggregates and shrinkage needs to be addressed:

- The aggregate acts as a restraint. Generally, increased aggregate content reduces the extent of shrinkage. *Comment: More aggregates will also give a "diluting" effect due to less cement per volume unit of concrete.*
- The type of aggregate itself may have some significance for the magnitude of shrinkage, because aggregate affects the E-modulus of concrete. Higher E-modulus generally gives lower resulting shrinkage.
- Some aggregates may shrink themselves. For example, some types of dolerite, greywacke, basalt and mudstone may give a much higher potential of shrinkage than concrete with granite, limestone and quartz aggregate.

If the same aggregate composition is applied in a laboratory performance test as in a real field concrete, none of these factors will significantly influence the lab/field correlation. However, for high performance concrete, the aggregate water absorption and moisture state may be of high importance, due to the assumed influence on the concrete internal RH (see 2.3.1).

2.4 Influence of binder type

2.4.1 Moisture content

Type of binder may influence the permeability of the concrete, and thus also the water uptake and the sensitivity to drying during exposure and measuring. The extent of self-desiccation, and as a consequence the internal RH, may also vary depending on type of binder. In addition, many binders containing SCMs will be more influenced by the curing – and storage temperature (see 2.2.1).

2.4.2 Self-desiccation (RH)

Different Portland cements may lead to different self-desiccation. An important parameter is the fineness (Blaine) of the cement. Generally, finer cements and higher amounts of

C_3A and C_4AF may lead to increased self-desiccation and autogenous shrinkage (Atlassi et al., 1991; Nilsson, 2002; Kvalvik et al., 2009).

The use of silica fume, fly ash and slag may increase the self-desiccation and thus reduce the internal RH, (Sellevold, 1988; Sellevold & Justnes, 1992), in particular if the prisms are sealed or partly sealed (e.g. "wrapped" with little access to sufficient water supply).

2.4.3 Shrinkage

The extent of shrinkage is dependent on the loss of moisture (drying shrinkage) and the reduction in the internal RH due to self-desiccation, as discussed earlier. Thus, the binder type is of importance for the magnitude of the total shrinkage that may occur, due to the influence on the concrete permeability and degree of self-desiccation (see 2.4.1 and 2.4.2). Justnes (2004) reviewed the influence of binder on autogenous shrinkage and chemical shrinkage.

2.5 Influence of mix design / casting

2.5.1 Moisture content

The sensitivity to drying during exposure and measuring will decrease with decreasing w/cm ratio, due to a reduced and refined porosity and as a consequence a reduced permeability. However, the ability to suck water will also be reduced with decreasing w/c, as shown by Kvalvik et al. (2009). The measurements showed that the internal RH in the concretes with w/c 0.40, in contrast to the concretes with w/c ratio 0.60, was almost independent of the curing conditions, which varied between the extreme points of water ponded on the top of the sample for seven days before the start of drying to no covering of the concrete surface after casting.

At low w/c it may be difficult to secure a sufficient high moisture content within the concrete due to a high degree of self-desiccation, in particular for rather massive concrete structures (e.g. outdoor stored cubes) and maybe also for rather large laboratory test specimens. For such structures/specimens the extent of self-desiccation may govern the interior RH level of the concrete, (Sellevold and Justnes, 1992; Lagerblad and Trägårdh, 1994; Stark, 1995; Ferraris, 1995; Nilsson, 2002; Hammer et al., 2004; Yang et al., 2005; Lura et al., 2007), and thus influence the extent of damage due to ASR. For example, in tests performed by Sellevold and Justnes (1992) the internal RH in sealed cement paste samples with w/cm ratio varying from 0.20-0.40 was in the range 80-90% after approximately two weeks of hydration. This is close to the critical limit for developing ASR (see 2.1.1).

The amount of water within an aggregate may have a considerable influence on the RH within the concrete, in particular for concretes with a low w/c ratio (see 2.3.1). During the curing period, the aggregate particles may supply the paste with water, thus counteracting the effect of self-desiccation, (Hammer et al., 2004), (Lura et al., 2007) and (Meddah and Sato, 2010).

2.5.2 Self-desiccation (RH)

The self-desiccation will increase with decreasing w/cm ratio, as also discussed in 2.5.1. Thus, the concrete RH may for some test arrangements be controlled by the w/cm ratio of the concrete, in particular if large prism sizes and water tight wrapping is applied. Due to this fact, a minimum limit should be considered for the w/cm. A suggestion for such a limit could be w/cm ≥ 0.40 – in other words, performance tests should not be conducted at w/cm less than 0.40.

According to Lagerblad and Trägårdh (1994), there could be differences for rapidly and slowly reactive aggregates with respect to the effect of w/b (tested according to NT Build 295, 1985). This implies that certain aggregate types simply need more moisture to react. Hence, too low w/b could, for certain aggregate types, give "false positive" response to the testing. For example, it is known that Norwegian sandstone is particularly sensitive to the moisture condition, (Wigum (editor), 1999). With the introduction of smaller containers for the Norwegian CPT, which resulted in increased RH within the container, the Norwegian sandstone, proven to be reactive in field, showed expansions above the critical limit (Wigum and Lindgård, 2008).

As discussed in 2.3.1 and 2.3.2, the water absorption of the aggregate is important. Consequently, it is of large relevance if the aggregates are wetted or not. The self-desiccation may be more or less eliminated, even for a low w/c concrete, if highly porous and wetted aggregates are used, according to Hammer et al. (2004), Lura et al. (2007) and Meddah & Sato (2010).

The curing time and the moisture conditions during curing (submerged or sealed or somewhat between) are of importance for the effect of self-desiccation and thus for the concrete RH. Submerged curing during the first weeks may counteract at least some of the effect of self-desiccation. The importance of moist curing increases with decreasing w/b, since less water is present in the concrete. However, for very low w/b concretes, even submerged curing may not give a sufficiently high internal RH in the concrete, as discussed in 2.2.2.

It is a question whether some chemical admixture types influence the self-desiccation of the concrete significantly and thus influence the concrete RH. No relevant literature was found on this topic.

Will Lithium influence the self-desiccation of the concrete?

In the paper by Millard and Kurtis (2008) this question is, among other factors, looked into. Some results indicate that lithium nitrate may accelerate early chemical shrinkage and hydration. Generally, as the lithium dose increased, less autogenous shrinkage was observed in the first 10 days. Often, a net expansion occurred in the first 24 h. After 28 days, pastes with the highest lithium content (four times the standard dose) exhibited significantly greater autogenous shrinkage than the control samples. However, in all conditions examined, pastes produced with the standard dose of lithium nitrate did not exhibit significantly more autogenous shrinkage than the corresponding control (no lithium) mixes. However, it is worth noting that one of the low-alkali cements, where early hydration was most accelerated by lithium nitrate addition, shows the least effect of lithium addition on autogenous shrinkage. Thus, further research is necessary to completely understand the relationships between hydration, microstructure development and autogenous shrinkage with the addition of lithium nitrate.

Overall, for most cement types, the results suggest that lithium nitrate admixtures are likely innocuous when used at recommended dosages. However, additional testing may be warranted to examine early setting, heat evolution, and shrinkage, for critical applications, particularly with low alkali cements. In general, however, variations in behaviour were greater between the six different cements than with increasing lithium nitrate admixture dosage for a particular cement.

No studies on other chemical admixtures have been revealed. Some of these may possibly, to a certain extent, influence the pore size distribution and the internal concrete moisture content.

2.5.3 Shrinkage

The autogenous shrinkage will increase significantly with decreasing w/cm ratio due to higher self-desiccation, see also 2.5.2.

The resulting drying shrinkage generally decreases with decreasing w/b ratio (at constant binder content). However, the potential shrinkage increases with increasing binder content. To achieve consistency, a decrease in w/b ratio is normally followed by increase in binder content. Hence, the net effect of decreased w/b may be an increased shrinkage potential.

According to Neville (1995), some chemical admixtures may increase the extent of shrinkage. Thus, in a concrete performance test the chemical admixtures used should be proven to not increase shrinkage of the concrete.

2.6 Summary of internal humidity

During laboratory performance testing, the internal moisture content within the concrete prisms is aimed to be very high, i.e. higher than in most real concrete structures. Thus, the prisms should be subjected to "worst-case humidity conditions" in the storage containers used. One main question is whether the test set up is able to secure a sufficiently high moisture level within the test specimens, regardless of binder composition and w/cm ratio in the concretes tested. For binders with high self-desiccation, e.g. binders with low w/cm ratio or binders with a high content of SCMs, this may be a challenge. As a result, the prism expansion may be reduced due to the lowered internal relative humidity (RH).

Other parameters that may increase the influence of self-desiccation, and thus contribute to maintain a rather low internal RH in the concrete prisms (even less than the critical RH needed for ASR to develop), are prism size (worse when increased), micro climate in the storage containers, length of pre-curing (reduced RH if prolonged due to a higher degree of hydration), permeability (less water uptake if low) and storage temperature (the degree of influence may vary dependent on the micro climate in the storage container). The aggregate porosity and the aggregate moisture state at the time of mixing may also be of importance, since use of rather porous and pre-wetted aggregates theoretically may totally counteract the effect of self- desiccation.

The test set up and the test procedures must also aim to avoid loss of water during storage and measuring. Important parameters in this respect are quality control (e.g. always use watertight lids), strict measuring procedures (measure quickly with as low moisture loss as possible), pre-cooling or not before measuring (the prisms will dry during cooling, because moisture will move from the warmer inner part to the colder outer parts) and storage temperature (the higher storage temperature, the more drying during cooling).
As a quality control, the mass of prisms should always be measured, evaluated and reported. If the mass increase during the test is too low, the test results should be questioned.

One important question has to be asked: *What is the most correct "reference length" to apply in ASR testing; the length after de-moulding, the shortest length after some shrinkage has occurred or the length after a pre-curing period?* The magnitude of the irreversible shrinkage will also influence this question.

3 Composition of the concrete pore solution

3.1 The importance of the concrete pore solution composition

Amount and effect of alkalis in the cement paste
The main contributor of alkalis to the concrete pore solution is usually the cement. In order to assess the total content of available alkalis present in a cement or concrete, it has become standard practice to express the alkali content in terms of "sodium oxide equivalent": $Na_2O_{eq} = Na_2O + 0.658\ K_2O$ (in weight percent). However, as shown by Leemann and Lothenbach (2008a; 2008b), concrete mixtures produced with cements having a similar Na_2O-equivalent but different K/Na ratios can expand considerably differently in accelerated laboratory tests (see also discussions in chapter 3.5). Consequently, the Na_2O-equivalent as a parameter to assess the potential reactivity of concrete mixtures might be misleading in certain cases. Still, a test series performed on CEM I (OPC) cement from one cement company (two different cement plants) of different K/Na ratios (3.0 and 1.25) did not confirm such a finding. These two products were designed for the same market and application segment, i.e. the samples had similar total alkali level (1.06 and 1.13, respectively), fineness, C_3A and sulphate content level, as well as strength properties (Bremseth, 2001).

In a given concrete containing reactive aggregates, the reaction potential for a damaging alkali-silica reaction is to a great extent influenced by the composition of the concrete pore solution with its function as a reaction partner for the reactive silica and as a supplier of moisture.

The content of alkalis, i.e. sodium (Na^+) and potassium (K^+), in the concrete pore solution plays a major role for development of ASR. In the first place, more Na^+ and K^+ lead to dissolution of more hydroxyl ions (OH^-) from $Ca(OH)_2$ to maintain equilibrium with the increased alkali concentration. For high pH pore solutions and at 20°C, $[Na^+] + [K^+] \approx [OH^-]$ because the quantity of other ions are insignificant compared to the concentration of alkali ions beyond the first 24 hours (Thomas and Bleszynski, 2000; Duchesne and Bérubé, 2001). The pH of the pore solution will thus increase. This higher alkalinity again leads to dissolution of more reactive silica (SiO_2) from alkali reactive aggregates. Secondly, alkalis will react with the dissolved silica forming alkali silica gel (ACI Committee 221, 1998).

Many concrete structures reported internationally which show deterioration due to ASR, were constructed using high-alkali cements. That is to say, in excess of 1% alkalis as Na_2O_{eq}. The alkali content of cement clinker may be differentiated into two generic types; alkalis which are primarily condensed as alkali sulphates on the surface of clinker grains, and alkalis which are locked into the crystal structures of the clinker minerals like calciumaluminates (C_3A) etc. Alkalis present as water soluble sulphates go into solution almost immediately, whereas alkalis locked into clinker grains become available to the solution more slowly during hydration of the clinker grains. The overall characteristic release rate will vary from one cement type to another, depending on the distribution of alkalis between rapid-release and slow-release sources, as well as on total alkali content (Glasser, 1992).

Available alkalis – critical pH – leaching of alkalis
The alkali concentration in the concrete pore solution depends not only on the alkali content in the main constituents (cement and any additions), but also on the level of available alkalis that to a high extent is controlled by kinetics and mechanisms of release and fixation of these alkalis in reaction products (Schäfer, 2004). Of the normally applied supplementary cementing materials (SCMs), tests performed by Schäfer (2004) showed

that ground-granulated, blast-furnace slag (ggbfs) only made an insignificant contribution to alkalis in the pore solution. The reduction in the alkali content in the concrete pore solution was approximately proportional to the amount of cement clinker replaced. Fly ash (FA) exhibited a similar behaviour up to approximately 28 days of age. However, beyond that age more alkalis were fixed in the hydration products as the hydration progressed further. By adding silica fume (SF), even more alkalis were fixed in the hydrates, and then at a very early age. However, later on some of these fixed alkalis were released to the pore solution again.

The degree of reaction of an aggregate is a function of the alkalinity of the pore solution. For a given aggregate, a critical lower pH-value exists below which the aggregate will not react. Consequently, ASR will be prevented by lowering pH of the pore solution under this critical level where the dissolution of alkali reactive constituents (silica) in the aggregates will be strongly reduced or even prevented, as discussed by Böhm and Baetzner (2008). This pH-value corresponds to a certain alkali threshold that is widely accepted that exists for initiating and sustaining ASR in concrete (Rivard et al., 2003). No "absolute" limit is defined, because the critical alkali content largely depends on the aggregate reactivity (Sibbick and Page, 1992). For most alkali reactive aggregates, the alkali threshold when applying CEM I cements is in 38ºC CPTs measured to be in the range 3-5 kg Na_2O_{eq} per m^3 concrete, lower for some rapidly reactive aggregates. However, due to alkali leaching from laboratory exposed samples, the true field alkali threshold may be significantly lower than the limit measured in the laboratory.

The majority of existing concrete prism tests applies alkali contents in the range 5.0-5.5 kg Na_2O_{eq} per m^3 when testing the alkali reactivity of aggregates. If the alkalinity is changed during the test, the expansion of the concrete prisms will be influenced. Boosting by adding NaOH or any alkalis released from some aggregates will increase the alkali content, while any alkali leaching will reduce it. Therefore, the outcome of accelerated laboratory tests may depend on the extent of leaching of alkalis, and so will the laboratory/field correlation. Some slowly reactive aggregates may thus be accepted as non-reactive when concrete prisms are stored in a high humidity for one year (Rivard et al., 2003). The long-term expansion could also be prematurely stopped due to alkali leaching (Duchesne and Bérubé, 2001).

For ordinary Portland cement, CEM I, Rivard et al. (2003) summarized from Duchesne and Bérubé (1995) and Taylor (1997), that approximately 42% of the cement alkalis are fixed in the hydrates, thus being unavailable for any leaching. A significant part of alkalis will also be incorporated in any reaction products due to ASR (Bérubé et al., 2000a). The remaining alkalis may potentially be leached out from the concrete during accelerated laboratory testing. The main mechanism for alkali leaching is excessive condensation of water on the prism surfaces (Rivard et al., 2003), leading to an outward diffusion of alkalis from the interior of the concrete. The degree of alkali leaching depends on various parameters such as prism size, storage conditions and concrete mass ratio. The main parameters influencing alkali leaching are further discussed in the chapters 3.2-3.5.

Alkali leaching may be a particular problem during performance testing, where the aim may be to document the alkali reactivity of certain concrete mixes containing alkali reactive aggregates. In such mixes, normally FA, SF or ggbfs are added to the concrete mix or blended with a Portland cement. It is generally accepted that the principle mechanism by which pozzolanic materials hinder ASR, is by lowering the quantity of available alkalis in the pore solution (Schäfer, 2004), and consequently reduce the concentration of hydroxyl ions in the concrete pore solution (Duchesne and Bérubé, 1994; Shehata and Thomas, 2000; 2002; 2006; Thomas and Shehata, 2004; Thomas et al., 2006). Since the alkali reactivity of various aggregates varies a lot, no general "safe" lower concentration of hydroxyl ions in the pore solution can be stated. However, in the literature this limit is by several authors reported to lay in the range 200-300 mmol/l (Diamond et al., 1981;

Kollek et al., 1986; Thomas, 1996; Rivard, 2003; Kagimoto et al., 2004; Thomas et al., 2006; Shehata and Thomas, 2006). These alkali concentrations correspond to pH-values in the range approximately 13.3-13.5.

Enrichment and concentrations of alkalis in concrete structures
In addition to the total content of alkalis in a concrete system, the level of alkali distribution will also be of interest. It has been suggested that moisture mobility through concrete can cause alkali metal salts to migrate and create temporary or permanent concentrations of these salts in some sections of the concrete structure. One example, of where this can occur is in foundation blocks where the tops are exposed, allowing water to evaporate from the surface (Concrete Society, 1987).

Nixon et al. (1979) have shown that alkalis can diffuse towards the surface of concrete on wetting and drying. Xu and Hooton (1993) reported in addition that constant humidity gradients, freezing/thawing cycles and electrical potentials can produce strong ion movements as well. More recently, electrical potentials are being applied to concrete during repair to stop or avoid rebar corrosion. If chloride ingress is the problem, the chlorides may be drawn out of the surface layer. If high extent of carbonation is the case, alkalis may be added to the system. In both cases, a re-alkalization is taking place and hydroxyl ions are created at the embedded steel reinforcement as a result of the cathodic half-cell reaction. This could generate significant local alkali enhancements, and thus initiate and sustain ASR (Sergi et al., 1991; Ali and Rasheeduzzafar, 1993; Ishii et al., 1996).

Rain is also expected to wash/leach alkalis over time from the concrete surface.

Recycling of alkalis – role of $Ca(OH)_2$
Various authors, (French, 1989), (Lagerblad and Trägårdh, 1992), following Power and Steinour (1955), have observed the phenomenon of recycling of alkalis during the alkali-aggregate reaction. The alkali gel formed within the aggregate particles changes composition when it comes in contact with the paste, and becomes richer in calcium, and releases alkalis to the pore water. The change in composition is caused by either dilution of the alkalis by a calcium compound from the cement paste or by a cation exchange reaction where calcium replaces alkalis. Lagerblad and Trägårdh (1992) suggest that the cation exchange reaction would cause the displaced alkalis to return to the cracks in the aggregate particles and no alkalis are consumed. According to this phenomenon, the reaction may theoretically continue until all alkali-reactive material is transformed into alkali-silica gel.

Recycling of alkalis is also occurring when silica fume is added to the concrete (Shehata and Thomas, 2000; Schäfer, 2004). In the early stage, silica fume reacts fast with the alkalis from the pore solution to form an alkali-silica-gel. The gel at the border of the silica grain reacts with available calcium to form C-S-H phases that have a low Ca/Si ratio and a high alkali binding capacity. Alkalis will be released by this reaction. Most alkalis are bound by the alkali-silica-gel in the silica fume particles and the additional low calcium C-S-H phases. However, as long as alkali-silica-gel exists inside the particle, it is driven to react with calcium. Alkalis will continuously be released into the pore solution and increase the alkalinity of the pore solution after 28 days up to 2 or 3 years (Shehata and Thomas, 2002). This means that after a fixation phase, at least parts of the alkalis become available for an alkali-silica reaction.

In addition to the available alkali content in the pore solution, also the amount of calcium hydroxide, $Ca(OH)_2$, plays an important role in alkali silica reactions, even though no general agreement exists in which way (Thomas, 2001). In his paper, Thomas discusses several stated hypotheses on the role of $Ca(OH)_2$, with focus on the ability of calcium to replace alkalis in the alkali gel, thus making more alkalis available for further reaction. This recycling of alkalis may lead to a further expansion of concrete due to ASR, even if the alkali concentration in the pore solution has reached a low and steady alkali concentration. This phenomenon has according to Thomas been documented both in laboratory tests and in real structures.

To sum up: The content of alkalis, i.e. sodium (Na^+) and potassium (K^+), in the concrete pore solution plays a major role for development of ASR. An increased alkali content leads to dissolution of more hydroxyl ions (OH^-) from $Ca(OH)_2$ and the pH of the pore solution increases. This higher alkalinity subsequently leads to dissolution of more reactive silica (SiO_2) from alkali reactive aggregates.

It has become standard practice to express the alkali content in terms of "sodium oxide equivalent" (Na_2O_{eq}). There is, however, some discrepancy in the literature whether cements having a similar Na_2O-equivalent, but different K/Na ratios, perform differently regarding ASR.

As the degree of reaction is a function of the alkalinity of the pore solution, a high degree of alkali leaching during laboratory testing will lead to a poor laboratory/field correlation.

The reported *fixation of alkalis*, alkalis not being available for alkali leaching, should be looked into further, along with the potential *enrichment and concentration of alkalis* in concrete structures. The issue of *recycling of alkalis* in the concrete should also be investigated further, as well as the main question of how to overcome the problem with *alkali leaching*. The feasibility of accelerated laboratory tests may depend on this.

3.2 Influence of storage conditions on leaching of alkalis

In this chapter, a review is made on the extent of alkali leaching measured when various storage conditions are applied during laboratory assessment of alkali reactivity. These storage conditions include variations in:

- Temperature during curing, exposure and measuring
- Humidity in the storage containers, i.e. storage of the prisms on grids above water, submerged or possible with external alkalis added to the system
- Wrapping / no wrapping of the prisms
- Prism size
- Type of container
- Storage time

Stanton (1940) reported that mortar bars and concrete prisms did not show excessive expansion when exposed to continual wetting or to wetting and drying cycles. Stanton only observed expansion and cracking when moist specimens were stored in sealed containers and protected from drying. He also recognised that excessively wet conditions would result in reduced expansion. According to Thomas et al. (2006), the problem of alkali leaching from specimens stored over water in sealed specimens was first reported by Blanks and Meissner (1946). 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.

Increased storage temperature increases the rate of reaction and results in increased levels of expansion at early ages. However, Fournier et al. (2004) studied deviations between the 38°C concrete prism test and the 60ºC accelerated concrete prism test. They verified that in the 60ºC test, the ultimate expansion was considerably lower, probably due to higher extent of alkali leaching (higher concentration of Na^+ and K^+ was measured in the water at the bottom of the storage containers) and changes in pore solution composition (higher concentration of sulphate in the pore solution at elevated temperature due to higher solubility of ettringite - see Figure 4 in chapter 3.4). As a result of the latter, the concentration of hydroxyl ions in the pore solution, and thus the pH, decreased resulting in a lower solubility of SiO_2. However, increased expansion occurred at earlier age at high temperature.

The observed increased extent of alkali leaching at elevated temperature is expected, since the diffusion increases with increasing temperature.

Tests performed by Bakker (1983) showed that the larger the cross-section of a concrete prism, the greater the expansion, which was interpreted as being caused by higher extent of alkali leaching for the smaller specimens. However, even for larger concrete prisms (cross-section $100x100mm^2$) alkali leaching cannot be neglected (Lindgård et al., 2008).

Alkali leaching seems to be more severe for small specimens. Sometimes wrapping is applied in order to decrease leaching, but there are also references showing that wrapping may decrease the expansion (Bérubé and Fournier, 1993; Bérubé et al., 1996; Lindgård, 2010).

Rogers and Hooton (1989) demonstrated that higher expansions were measured when mortar bars (ASTM C 227, prism size $25·25·285\ mm^3$) were stored in containers without wicks (lining) instead of sealed in polyethylene bags.

Similar they found (Rogers and Hooton, 1991) that concrete prisms (CAN3-A23.2-14A-1986; assumed prism size 75 mm cross section) stored in a moist room showed the least expansion, as well as the greatest amount of alkali leaching. Storage in a poly-ethylene bag resulted in less leaching of alkalis and more expansion. They claimed that excessive condensation of water on the surface of the concrete can remove alkalis from the concrete, reducing the rate of reaction and expansion. Results of percent change in alkalis at 130 weeks of exposure exhibited;

- 22% decrease for prisms stored at 23°C in plastic bag with 100 ml of water
- 42% decrease for prisms stored at 38°C over water in sealed box
- 63% decrease for prisms stored at 23°C in humid room
- 128% increase for prisms stored at 23°C immersed in 5% NaCl

Rivard et al. (2003) demonstrated that significant alkali leaching occurred in the Canadian standard CSA A23.2-14 concrete prism test (prism size $75·75·300\ mm^3$) when tested at 38°C, even though prisms were covered with plastic sleeves which were closed at the top and loose at the bottom. By measuring the extracted pore solution, it was shown that after 52 weeks, the alkali concentration $[Na^+ + K^+]$ decreased by 22% and 24% for "Spratt mass and structural concrete", respectively, and 30% and 45% for "Potsdam mass and structural concrete", respectively. These values were based on the assumption that when calculating the total percentage reduction of alkalis, a certain proportion of the alkalis (42%) were subtracted from the total alkali content because of their fixation in the cement hydrates (i.e. the reported values are recalculated values). It was also found that leaching is not significantly influenced by the thin cracking network that occurs in laboratory test specimens. However, the reaction rate certainly has an effect on the rate of alkali consumption, as well as alkali leaching.

In a later study by Rivard et al. (2007), they showed that the condensation of water on mortar or concrete surfaces induces alkali leaching of ionic species dissolved in the concrete pore solution. The chemical analysis of the water beneath test prisms highlighted that the alkalinity reduction of the concrete pore solution with time mostly was associated with alkali leaching. It was shown that for the same reactive mixture, concrete alkali leaching seemed to be greater for the specimens containing higher alkali level (5.25 $kg/m^3\ Na_2O_e$) compared with specimens with lower alkali level (4.00 $kg/m^3\ Na_2O_{eq}$).

Results were presented for alkali leaching after 52 weeks of exposure. Based on previous calculation, i.e. a certain proportion of the alkalis are fixed in the cement hydration, it was found that alkali leaching after 52 weeks was in the order of 22-45%, highest for specimens with originally highest alkali content.

It is stated by Thomas et al. (2006) that the maximum alkali content that can be tolerated in the concrete without causing damaging expansion is a function of the reactive aggregate type. Experiences have shown that a higher level of alkali is required to initiate expansion in the concrete prism test than in real structures or large concrete blocks produced with the same aggregate and stored in field conditions. The need to boost the alkali content in concrete prisms means that the CSA A23.2-14 concrete prism test is not an effective means for determining the threshold alkali level necessary to produce deleterious expansion with a particular aggregate nor is it suitable to evaluate the ASR potential for a specific combination of materials (i.e. a "job mixture"). Clearly specimen size has a large impact on expansion and this effect can be largely ascribed to more leaching of the alkalis from smaller specimens. In their study they found that the impact of alkali leaching will be less for larger concrete prisms, but is still significant. Three concrete prisms ($75 \cdot 75 \cdot 300$ mm^3) containing a reactive siliceous limestone (Spratt) were stored over water at 38°C in a container. By assuming a constant reservoir volume of 1.8 l and neglecting any alkalis that may wick up the absorbent material lining the container, it was estimated that approximately 35% of the alkalis originally in the concrete found their way into the water reservoir after 1 year, and as much as 20% after just 90 days.

A study by Bokern (2008) focused on the laboratory testing regarding ASR and how preconditions during the induction phase (i.e. curing period) can affect the deleterious ASR. The effect of alkali leaching and pore solution alkalinity was investigated for three different storage conditions: firstly according to RILEM AAR-4.1 (RILEM, 2006; 60°C prisms of size $70 \cdot 70 \cdot 140$ mm^3 above water in a stainless steel container, designated "Ü60"), secondly according to the German Alkali Guideline in a 40°C fog chamber (cubes with 100 mm side length, designated "NK40") and thirdly according to a newly developed regime reflecting an outside storage (cubes with 100 mm side length, designated "SAL") as performed at the research institute of the German Cement Works Association (VDZ). In order to measure leaching of alkalis, either into the water bath below the specimen or into the water dropped from the specimen into a stainless basin (fog chamber), a sample was taken and the total water quantity was gravimetrically determined. In addition, pore solution was squeezed out. During all storages, a significant decrease in the potentially effective K-content (designated "K_{pot}", i.e. content of potassium) in the concrete specimens was found, meaning that alkali leaching occurred. Even during the simulated outside storage (SAL), about 15% of the K introduced by the clinker portion disappeared after 90 days, a portion of roughly 5% within the first 7 days. At the same time there were no considerable differences caused by the cement type. This changed for storage NK40 and Ü60. Whereas K_{pot} for CEM II/A-D and CEM II/A-V was about the same range as mentioned above, after 91 days the loss was about 41% (NK40) and 37% (Ü60), respectively, for the concrete specimens made of CEM I cement. For the specimens with CEM II/A-S, a loss of about 30% could be assumed if the temporary defect of the vaporizer is neglected (actually K_{pot} was 20% less than initially introduced).

According to Bokern (2008), extremely humid conditions like in a fog chamber with temperature 40°C can firstly lead to a dilution of the pore solution by water uptake of the specimens, especially at early ages (independent of cement type). Vacuum pressure created by cement hydration (i.e. due to self-desiccation) can be seen as a reason for that. Secondly, and on top of that, under such conditions intensive alkali leaching occurs. A loss of 20% of the initial soluble alkali content after 28 days and more than 30% after 90 days is possible for a concrete with CEM I cement and w/c ratio 0.55. Concrete made of OPC or cement with slag (20%) seems to be particularly vulnerable. Storage above water appears to be more suited in this respect for early ages up to 28 days (Ü60). But for later ages, when the water balance is achieved in the storage containers, alkali leaching reaches comparable ranges (30%).

In a study by Ideker et al. (2010), alkali expansions were measured in the concrete prism test (38°C) and compared with results from the accelerated concrete prism test (60°C). Prisms in both the tests (size $75 \cdot 75 \cdot 300$ mm^3) were stored in plastic buckets inside large walk-in ovens with circulating fans to move the hot air efficiently inside the oven. By pore solution analysis it was found that at later age the higher temperatures promoted increased leaching at 60°C.

In a recent project by Wigum (2010), the effect of alkali leaching was examined in the RILEM AAR-4.1 method (RILEM, 2006; unwrapped prisms of size 75x75x285 mm^3 stored at 60°C above water in a stainless steel container). A total of 12 different concrete compositions were tested, with various types of Icelandic aggregates and various types of cements (high alkali cement with no pozzolanas, low alkali cement, high alkali cement with 4% silica fume and high alkali cement with 6% silica fume and 3% rhyolitic pozzolanas). After 20 weeks of exposure, measurements were carried out on the alkalis (Na_2O_{eq}) in the water reservoir beneath the concrete prisms in the stainless steel container. The calculated results revealed amounts of leaching in the order of 2-10% of the originally alkali content (Na_2O_{eq}) in the concrete compositions.

In order to collect reliable leaching data in laboratory testing, a recommended test procedure for how to sample and how to measure the alkali content in collected samples, is given in Appendix 8.

In contrast to many laboratory results, pore solutions in field concrete are mostly not subject to alkali leaching (Rivard et al., 2007), probably due to the higher volume to surface ratio compared to laboratory specimens. The problem with alkali leaching is thus a big challenge in laboratory tests.

To sum up: Only a limited number of papers have quantitatively reported the extent of alkali leaching revealed with various concrete prism methods. Thus, more research is needed to contribute data in this area. Research studies have however revealed cases where up to 35% of the alkalis originally in the concrete found their way into water reservoir after 1 year (Thomas et al., 2006), while other studies present alkali leaching in the order of 2-10% of the original alkali content (Wigum, 2010; Lindgård, 2010). It is also revealed that alkali leaching is highest for specimens with the highest original alkali content.

It is clear that various storage conditions will influence the amount of alkali leaching, and potentially synergic effects between various conditions may occur. In particular the *prism size,* the *storage temperature* and any application of *wrapping* of the prisms may have a major influence on the extent of alkali leaching. Another issue of interest for further research is the extent of alkali leaching vs. the concrete *alkali content*.

3.3 Alkali release from aggregates

Some aggregate types may release alkalis to the concrete pore water (Grattan-Bellew, 1994; Bérubé et al., 2000; 2002; Constantiner and Diamond, 2003). Bérubé et al. (2000) tested the extent of alkali release for 17 aggregate types from Canada. Most of these aggregates contributed with alkalis in the range 0.45 to 0.70 kg Na_2O_{eq} per m^3 of concrete, but the amount varied from about 0.1 to 1.6 kg Na_2O_{eq} alkalis per m^3 of concrete dependent on aggregate type.

Ideker et al. (2010) showed that the contribution of alkalis from a “non-reactive” sand resulted in increased concentration of K^+ in the pore solution, elevated pore solution pH and a higher rate of expansion at early age compared to other “non-reactive” sands tested. The difference was most pronounced for the 60°C CPT.

The influence of w/b ratio, alkali boosting and pH on the extent of alkali release is discussed in chapter 3.5.

Broekmans (2010) has recently performed a review on alkali release from aggregates and discussed alkali leaching from concrete prisms. Some of his findings are quoted in the following: “Release of alkalis, Na^+ and/or K^+, is a matter of extensive dispute, in concrete structures suffering from deleterious ASR as well as in testing and assessment of aggregate materials for use in concrete. In existing concrete, a number of aggregate lithologies have been suggested to release poorly bonded alkalis from certain minerals, e.g. K-feldspar in particular if altered to sericite or kaolinite, muscovite, illite, and others. The efficacy of water-soluble inhibitors like Li-salts added to the concrete mix that potentially could pervade into the interstitial pore space in the aggregate is unknown.

The weak bonding character of Na^+ in silicate minerals and glasses is well illustrated by the fact that assessment by EPMA (and especially SEM-EDS without mineral standards) requires special precautions and instrument setup to compensate for the volatilization of Na under the incident probe beam (Morgan & London 1996, 2005).

Alkali release from rock forming minerals exposed to ‘concrete conditions’ (either simulated or in real life) has been investigated extensively by many, e.g. Diamond et al. (1964), Bérubé et al. (1988, 1990, 2002) and many more (see appended literature list). Alkali release from rock forming minerals under natural conditions has been studied extensively as well. The volumes by Hochella & White (1990) and White & Brantley (1995) present state of the art reviews and a wealth of literature references.”

The task group “Releasable alkalis” in RILEM TC 219-ACS is presently trying to develop a reliable test procedure to measure the extent of alkali release from various aggregate types.

3.4 Influence of binder type

In the <u>cement clinker</u>, K^+ and Na^+ are present as sulphates and in the silicate and aluminate phases. The sulphate ions anions (SO_4^{2-}) form ettringite and AFm phases at early ages and some sulphate is bound in C-S-H. As a result, equivalent amounts of OH^- anions go into solution (Taylor, 1990) to maintain electro-neutrality (i.e. to balance the alkali cations). Just after setting, the concrete pore solution contains sulphate, calcium and alkali hydroxides. The solution concentration becomes stable within 48 hours with a stable mixture of sodium and potassium (and a low amount of calcium) hydroxides. Thus, the composition of pore solution of cement is mainly dependent on the alkalis available in the clinker, while the pore solution alkalinity decreases by ongoing ASR (Poole, 1992). The contribution of <u>alkalis from supplementary cementing materials (SCMs)</u> to the pore solution is another question.

Increasing the alkali level of cement clinker will also lower the CaO concentration and increase the SiO_2 concentration of the pore solution (Taylor, 1990). The cement alkalinity also affects the behaviour of SCMs in reducing the ASR expansions even though their total binder contents are the same.

Regarding ASR, <u>alkali binding capacity of hydration products</u> is of importance, because it has a strong influence on the composition of the pore solution and thereby on the alkali-silica reaction in concrete compositions. Alkali binding capacity is further discussed in chapter 4.1.

Some SCMs can also release alkalis to the pore solution, such as ground granulated blast furnace slag (ggbfs). The extent is much less than that of clinker, and is almost independent of the alkali content of the ggbfs. The alkalinity of the pore solution of ggbfs containing cements is mainly attributed to the reduced clinker content of the cement. In cements with ggbfs, alkalis are mainly adsorbed by the C-S-H phases. Up to 40% ggbfs, the Ca/Si ratio of the C-S-H phases and therefore also the sorption properties are similar to that of OPC (Schäfer, 2004).

Depending on its inclusion level, silica fume (SF) incorporation decreases the Na^+, K^+ and OH^- ion concentrations in the pore solutions of pastes and concretes containing reactive aggregate. Silica fume inclusion increases the Na^+ and K^+ content of C-S-H of the hydrated cement paste (Cheng Yi and Feldman, 1985). Silica fume reacts fast with the alkalis from the pore solution to form an alkali-silica-gel (Shehata and Thomas, 2000). Thus, the alkali concentration in the pore solution decreases within the first two days of hydration (Schäfer, 2004). The Ca/Si ratio of C-S-H was found to be 1.70 for cements containing 25% slag and 1.43 for those containing 5% silica fume (Durand et al., 1990). The gel at the border of the silica grain reacts with available calcium to form C-S-H phases that have a low Ca/Si ratio and a high alkali binding capacity. Alkalis will be released by this reaction. Most alkalis are bound by the alkali-silica-gel in the silica fume particles and the additional low-calcium C-S-H phases. However, as long as alkali-silica gel exists inside the particle, it is driven to react with calcium. Alkalis will continuously be released into the pore solution and increase the alkalinity of the pore solution after 28 days up to 2 or 3 years (Shehata and Thomas, 2002). This means that after a fixation phase, at least part of the alkalis become available for alkali-silica reaction.

It has been shown that high-CaO fly ash (FA) is not as effective in reducing the pore solution alkalinity of cement paste. In an extensive study investigating the effect of several types of fly ashes of North America in various amounts by using concrete and mortar bar expansions tests, Shehata and Thomas (2000) concluded that the minimum level of replacement required to control expansion is increased as the calcium or alkali content of the fly ash increased or as its silica content decreased. In FA-containing cements, the alkali fixation in the resulting reaction products starts at the same time as the pozzolanic reaction after a period of approximately 28 days, which results in a successive reduction of the dissolved alkali content. Low-CaO FA reduces the pore solution alkalinity beyond just dilution (Schäfer, 2004). Due to the pozzolanic reaction, the C-S-H phases are low in calcium and have a high alkali binding capacity. The fly ashes that were found to be most effective in reducing the alkalinity of the pore solution expressed from paste samples were also found to be the best for controlling ASR expansion (Shehata et al., 1999). Sibbick and Page (1995) stated that the effectiveness of the FA's in suppression of ASR was dependent on the initial alkali content of the mix and on the alkali content of the FA, but the results of pore solution analysis did not provide a simple explanation for the corresponding expansion data showing that the differences in expansions cannot *only* be explained by changes in the pore solution chemistry (Sibbick and Page, 1995). Thomas et al. (1997), following an overall survey, differentiates with respect to quality parameters of the SCM: Limiting the total alkali content of the slag and fly ash to 1.0% and 4.5%, respectively (and some additional limitations), the alkali contribution from the SCM may be assumed to be zero, in spite of some contradicting laboratory conditions test results.

Figure 2 shows an empirical relationship between the OH^- concentration of the pore solution extracted from 2-year-old sealed pastes with w/cm = 0.50 (Thomas and Shehata, 2004; Thomas and Folliard, 2007) and a “chemical index” derived from the chemical composition of the binder. A total of 79 different binders were tested including the following:

- 100% Portland cement at a range of different alkali contents (0.36 to 1.09% Na_2O_{eq})
- Binary mixes with 25 to 70% fly ash using 18 different fly ashes with a range of chemical compositions (1.1 to 30.0% CaO, 1.4 to 9.7% Na_2O_{eq})
- Binary mixes with 25 to 50% slag, 5 to 10% silica fume and 10 to 20% metakaolin; each SCM came from a single source
- Ternary mixes containing silica fume blended with either slag or fly ash; both low-calcium and high-calcium fly ash were used

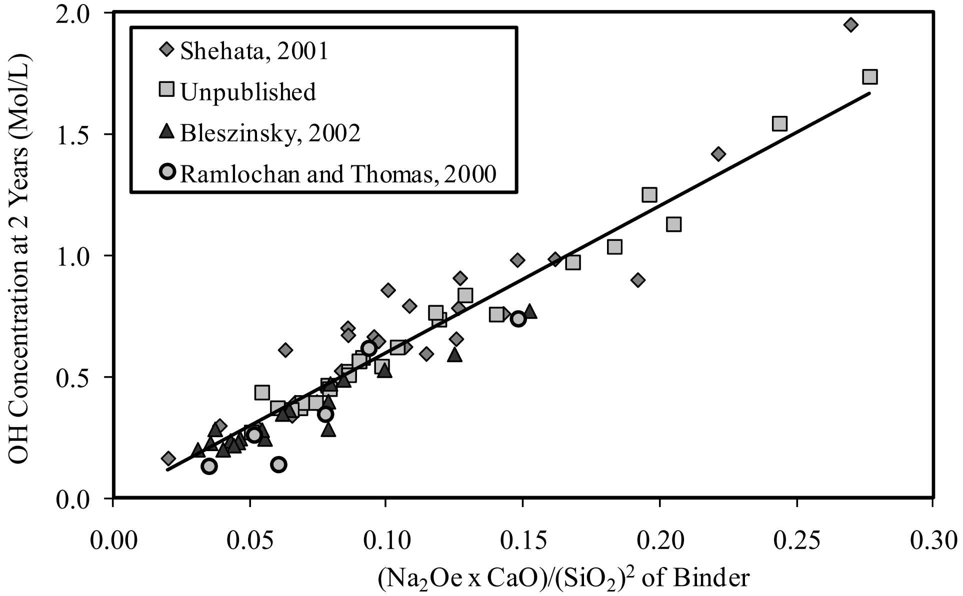

Figure 2 Relationship between pore solution composition and the chemical composition of the binder

The relationship shown was derived empirically to find the “chemical index” that was most reliably correlated to the OH^- concentration based on a least-square fit. The best-fit index was found to be the product of the equivalent alkalis and calcium divided by the square of the silica content of the binder $(Na_2Oe \times CaO)/(SiO_2)^2$. Although this is an empirical relationship it makes sense intuitively because the alkalinity of the pore solution can be expected to be a function of the alkalis in the binder and the ability of the hydrates to bind alkalis which has been shown to be a function of the calcium-to-silica ratio of the binder (see discussion below). The alumina content of the binder was not found to be statistically significant based on the empirical analysis conducted using this dataset, despite the apparent benefit of alumina demonstrated by Hong and Glasser (2002). They showed that introducing alumina into C-S-H, to form C-A-S-H, markedly increases its alkali-binding capacity, and they suggest that this partially explains the beneficial effects of aluminous SCM with regards to reducing pore solution alkalinity and the potential for ASR.

The alkali boosting in laboratory specimens by adding the alkalis to the concrete mix water to accelerate the ASR affects the pore solution chemistry. Diamond (1997) stated that the alkali boosting did not reveal an increased hydroxyl ion concentration as expected, however, the sulphate concentration is increased which he claims may lead to delayed ettringite formation. If so, this is expected to affect the correlation between laboratory and field expansions.

The cement type or binder combination influences the permeability of the concrete compositions, and thereby the rate of alkali leaching. Recent investigations by Schmidt (2009) show that the extent of alkali leaching during ASR-testing at 40°C is influenced by the binder combination (Figure 3). Naturally, this will influence the measured expansions. A direct comparison of the effect of different cement types or cements with different SCMs on avoiding a damaging ASR is therefore not possible on the basis of a general limit value for expansion and crack width development.

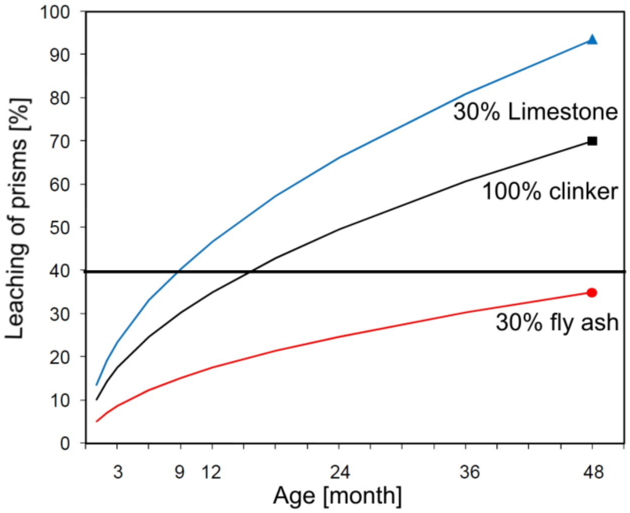

Figure 3. Estimated development of alkali leaching of concrete prisms with different binders, 400 kg/m³ of binder, w/c = 0.45, storage at 40°C and 100% RH in a fog chamber (Schmidt, 2009).

Similar to what Fournier et al. (2004) and Lothenbach et al. (2007) have shown earlier, Schmidt et al. (2009) have recently documented that the concentration of sulphates in the pore solution is increased when elevating the storage temperature, see Figure 4. Thus, the concentration of OH^- is reduced correspondingly. Primarily as a result of the drop in OH^- concentration, addition of only 10% fly ash to the binder was apparently able to suppress the expansion below the critical expansion limits for a highly reactive aggregate when exposed to 60ºC one day after casting. When pre-cured at 20ºC for at least 28 days before starting the 60ºC CPT, the concrete prisms expanded far beyond the critical limits. Also when adding 20% fly ash, the effect of the length of the pre-curing period on the measured prism expansions was significant, but less pronounced. When adding 30% fly ash, no expansion was revealed for any of the three pre-curing periods applied (1, 28 and 90 days, respectively).

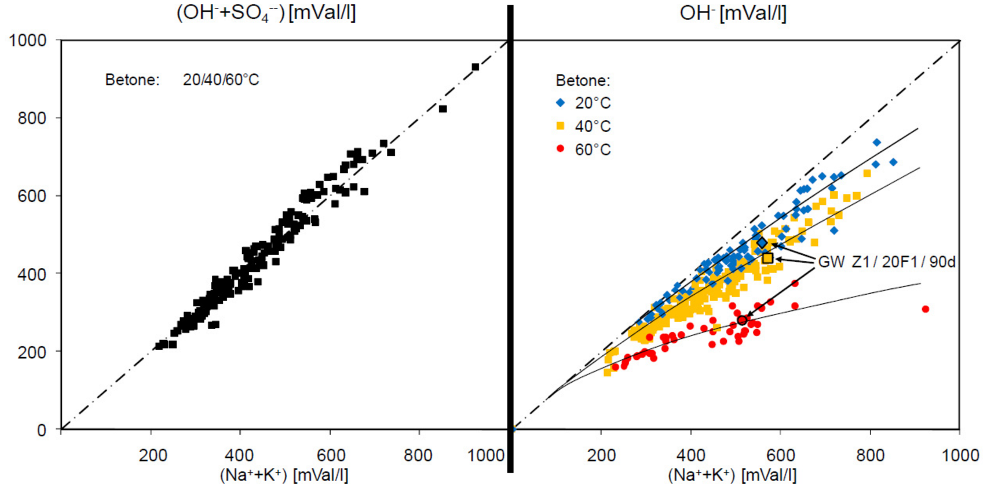

Figure 4: Concentration of anions OH$^-$ and SO$_4^{2-}$ vs. concentration of cations Na$^+$ and K$^+$ of pore solutions at different temperatures (Schmidt et al., 2009).

To sum up; The binder type is influencing the composition of the concrete pore solution that is mainly dependent on the alkalis available in the clinker. Low-CaO fly ashes reduce the pore solution alkalinity beyond mere dilution, whereas ground granulated blast furnace slag (ggbfs) can release alkalis to the pore solution. The extent is much less than that of clinker, and is almost independent of the alkali content of the ggbfs. Silica fume reacts fast and decreases the alkali concentration in the pore solution within the first two days of hydration, whereas the alkali concentration increases after 28 days up to 2 or 3 years, due to a reaction of calcium with the alkali-silica-gel and a release of alkalis in the pore solution.

The storage temperature and the length of the pre-curing period at 20°C may have a significant influence on the outcome of a performance test, in particular when SCMs are present. Both Fournier et al. (2004) and Schmidt et al. (2009) have documented that the concentration of sulphates in the pore solution is increased when elevating the storage temperature. Thus, the concentration of OH$^-$ is reduced correspondingly. Primarily as a result of the drop in OH$^-$ concentration, addition of only 10% fly ash to the binder was apparently able to suppress the expansion below the critical expansion limits for a highly reactive aggregate when exposed to 60ºC one day after casting (Schmidt et al., 2009). When pre-cured at 20ºC for at least 28 days before starting the 60ºC CPT, the concrete prisms with 10% fly ash expanded far beyond the critical limits.

The cement type or cement-SCM-combination influences the permeability of the concrete and thereby the rate of alkali leaching, the development of the OH$^-$ concentration of the pore solution during testing and the rate of expansion.

The rate of alkali leaching is much higher in small test specimens compared with massive concrete blocks or real structures in the field. This will influence the laboratory/field correlation.

3.5 Influence of mix design / casting

For details, see Appendix 3.5.

Chapter 3.5, Appendix 3.5 and the corresponding part of the Table in Appendix 1 provides considerations of how the concrete mix design in a performance test could influence the laboratory/field correlation. Most of the considered parameters have only minor or no influence on the laboratory/field correlation. Some will only have an influence if the concrete composition that is going to be tested is modified or changed compared to the job mixture. In the following, some considerations regarding the most important parameters based on the Table in Appendix 1 are discussed briefly.

Considerations regarding w/b ratio

Increasing w/b ratio will result in a higher porosity (increasing the amount of capillary pores) and consequently internal transport processes will be accelerated, alkali leaching will increase and water or possibly other solutions will penetrate more easily (Kamali et al., 2003; Kamali et al., 2008). With decreasing w/b ratio the content of hydration products decreases and the hydration products tend to become more homogeneous and contain less crystalline hydrates, particularly portlandite. At very low w/b ratios, some of the portlandite may occur in nanometre dimensions rather than in well crystallized form (Locher, 2000; Slamecka et al., 2002). A decreasing w/b ratio increases the OH^- concentration in the pore solution and vice versa (Stark et al., 2008).

The amount of alkalis released from certain aggregates depends mainly on the type of the aggregates (see also chapter 3.3). However, with decreasing w/b ratio, the pH increases and also the release of alkalis from aggregates increases due to the stronger attack, i.e. due to the increased solubility of alkali-minerals at high pH. Contradictory; the major factor that influences the maximum alkali release is the pore solution/aggregate ratio. In a dense paste (low w/b ratio), transport and ingress of water or solutions, respectively, is reduced as well as the release of alkalis from aggregates (Wang et al., 2008).

A reduced w/b ratio will also reduce the internal RH in the concrete due to increased self-desiccation (see section 2.5.2).

Considerations regarding air content / air entrainment

Air entrainment is important for concretes exposed to freeze-thaw cycles and de-icing solutions. In the literature, contradictory conclusions with respect to influence of the concrete air content of the ASR expansion are reported by Hobbs (1988), and Fournier et al. (2008) and Touma (2001) (see also discussions in chapter 4.4 and 6.4). The expansion of concrete made with fine reactive opaline silica particles with a size of 150 to 300 µm was reduced about 40% by air-entrainment (Hobbs, 1988). Also the results from air entrained and non-air-entrained concrete block that were made with coarse as well as fine reactive aggregates and that were stored in outdoor exposure sites show that air-entrainment might reduce expansion for some aggregates. But with other aggregates, the expansion was even higher.

Unpublished results from VDZ show that air-entrainment has no significant effect on concrete expansion if tested in the 40°C-fog chamber or according to RILEM AAR-4.1 60°C CPT (RILEM, 2006). These data show that air-entrainment does not have a clear effect on ASR expansion and is not able to prevent a damaging ASR in concrete. The results indicate that the effect is different for different types of aggregates. No relevant literature about the influence of air-entrainment on alkali leaching could be found.

Experiences from performance tests at the FIB for pavement concretes with mainly slow/ late reactive aggregates and usually 4-6% air have shown that a higher air void content does not reduce expansion due to ASR. But since ingress and transport of solutions is supported by freeze-thaw cycles leading to an increasing degree of saturation with every cycle far above isothermal saturation level (Setzer, 2001; 2002), freeze-thaw cycles were included in the FIB performance test (Stark et al., 2008) for air-entrained concretes that are subjected to freeze-thaw and de-icing salt attack in the field, e.g. pavement concretes.

Considerations regarding binder / cement content
With respect to ASR, the cement content influences mainly the alkali level in the concrete. Higher cement content will result in a higher alkali level which is often desirable for aggregate testing (e.g. RILEM AAR-3) to meet the worst-case and to compensate for alkali leaching effects. But higher cement content compared to the job mixture might change several concrete properties and consequently the laboratory/field correlation. Higher cement content results in a greater portion of paste in the concrete which influences transport processes since they take place mainly in the paste and the interfacial transition zone (ITZ), respectively. Higher cement content also increases the amount of hydration products, especially $Ca(OH)_2$ which plays a major role in ASR regarding gel formation and in the process of exchanging alkalis from the gel for calcium (Thomas, 1998; Diamond, 2000).

It is often argued, that a somewhat (up to 5 wt.%) higher cement content should be used to consider cement dosage fluctuations during concrete production. However, the dosage accuracy of a typical mixing plant is ± 1 wt.% and consequently even lower than the 3 wt.% limit allowed according to the standards (e.g. DIN EN 206-1). So there seems to be no need to increase the cement content for a performance test to consider dosage fluctuations. For composite cements with fly ash or slag (ggbfs) as well as for combinations of CEM I and SCMs (binders), higher binder contents even could be counter-productive, since a higher amount of SCM in the concrete could result in an overestimation of the effectiveness of the SCM compared to field performance.

Increasing the cement or binder content will also reduce w/c or w/b, which can lead to an increase in self-desiccation (see section 2.5.2).

Considerations regarding alkali boosting
For ordinary concrete prism tests, i.e. aggregate tests, it is common to increase the alkali content (alkali boosting) by addition of NaOH to (1.) meet the worst-case in alkali content and (2.) to compensate for alkali leaching effects. However, it is doubtful if boosting is an adequate method for a performance test, since boosting does not allow to determine the so called “alkali threshold”, i.e. the highest alkali content possible for a certain aggregate without causing deleterious ASR. The effect of alkali boosting on expansion also depends on the type of aggregate. Some aggregates are more sensitive to alkali boosting than others (Fournier et al., 2008). Also, depending on the type of the alkali compound added, boosting might initiate different mechanisms (e.g. DEF due to boosting with alkali sulphates) that will not appear in the field and consequently influence the laboratory/field correlation (Chatterji et al., 1987).

The addition of NaOH to the concrete mix will possibly accelerate the release of alkalis from certain aggregates due to the increased attack of the alkali-minerals at high pH (Bérubé et al., 2002; Bérubé and Fournier, 2004; Lu et al., 2006d; Wang et al., 2008). Also the type of the alkali ions (Na^+ or K^+) and the source influence the release of the alkalis.

The K/Na ratio might be important too, because different gel compositions result in different expansion behaviour (Leemann and Lothenbach, 2008a; 2008b) – see also chapter 3.1. Even more important, the solubility of $Ca(OH)_2$ is decreased in alkali hydroxide solutions, i.e. the Ca concentration in the pore solution will be lowered, but some Ca is required for the formation of swelling gels (Wang and Gillott, 1991; Stark et al., 2008; Stark et al., 2010). Experiences (unpublished data) with mortar bar tests at the FIB show clearly that alkali boosting mortars with cements (CEM I) different in Na_2O_{eq} to the same alkali level by adding NaOH does not result in the same expansion. Further-more, boosting is not appropriate to consider mechanisms triggered by externally supplied alkalis that may occur in pavement concretes, particularly the mechanisms caused by deicers based on alkali acetates and formates which increase the solubility of $Ca(OH)_2$ (Stark et al., 2008; Stark and Giebson, 2008; Giebson et al., 2010a).

In general, alkali boosting should be avoided for a performance test. However, performance testing must consider variations in the cement alkali content during cement production. A cement batch with the highest alkali content possible during production should be selected for the performance test, but a suitable batch may not be available at the time of testing. This could be considered by limited boosting, i.e. the addition of a certain quantity of alkalis to meet the highest possible alkali content of the cement that can occur during the production. Discussions during the meetings of RILEM TC-219 ACS within the task group "performance testing" led to the conclusion that more research is needed to decide how this issue can be treated best. A first set-up for investigations has been drafted and will include different concrete tests (RILEM AAR-3, FIB cyclic climate storage) as well as basic investigations (pore solution analysis).

It should be noted, that the issue of material property fluctuation is important for all concrete raw materials. For a construction project, many tons of cement, aggregates etc. will be used, but the material properties (e.g. cement alkali content, reactivity of the aggregates) will fluctuate more or less during the construction period. Experiences at the FIB with performance testing show that the reactivity of the aggregates can be monitored by running mortar bar tests over the construction period and compare the results with the results for the aggregate batches used for the performance test.

Considerations regarding curing

For aggregate tests, e.g. RILEM AAR-4.1 (RILEM, 2006) and German fog chamber method (German Ausshuss für Stahlbeton, 2001), not much attention is paid to curing. The prisms are usually de-moulded one day after casting and the test starts shortly thereafter. But curing becomes more important for a performance test, especially when testing concretes with SCMs. With increasing curing time, temperature and RH, the hydration degree of the binder will increase, hence the paste will become denser, alkali leaching will be reduced, but the ingress of water and (possibly) de-icing solutions will also be reduced (Stark et al., 2008; Giebson et al., 2010b). Performance testing with the cyclic climate storage at FIB already considers such aspects by pre-storing prisms made from OPC concretes for 7 days and from SCM-containing concretes for 28 days or even longer. For special cases, the nature and duration of curing is adjusted for the specific project, e.g. for precast elements which may be installed and put in to service several months after casting. Depending on the type of the binder and the building purpose, the prisms for a performance test should be cured more carefully, i.e. more realistic of field conditions (see also chapter 2.2, 3.4 and 4.1).

Other aspects

Another aspect regarding mix design are chemical admixtures that should be used in the laboratory testing as intended in the field. However, in real life different concrete producers will apply different types and varying amounts of chemical admixtures. It is not feasible to test all these variants, thus the assumed worst-case variants (e.g. with the highest alkali content) should be tested.

General FIB considerations and recommendations

Probably no individual performance test procedure will be able to evaluate all concrete mixtures and consider all aspects of different service requirements and environmental conditions in the field. For example, hydraulic structures are planned to be in service for about 100 years, they are exposed to freshwater only and depending on the location, they are exposed to freeze-thaw cycles, but not to external alkalis. The situation is different for other structures, e.g. for pavements which are large-area structures planned to be in service for 30-50 years. Pavements are exposed to very severe conditions such as de-icing salts, freeze-thaw cycles and traffic loads. The mix design and the service conditions for a dam and a pavement will be different and consequently also the progress of ASR will be different. It seems possible that different exposure conditions will demand for different or at least for modified performance tests. A single "worst-case and fits-all" test is not a contemporary approach with respect to a sustainable building philosophy. It must be highlighted once more, that a performance test is not for assessing single concrete components, e.g. the reactivity of aggregates, but it is for assessing the job specific concrete mixture under accelerated but realistic as possible exposure conditions (Stark et al., 2008; Seyfarth et al., 2009a; 2009b; Stark et al., 2010, Giebson et al., 2010a). Hence, for a performance test, the same mix design and casting parameters should be used as intended for the job mixture. If the real job mixture is tested with the performance test, the mix design parameters alone will have no or only minor influence on the laboratory/field correlation.

Summary
Based on the literature survey performed (see Appendix 3.5), the following conclusions can be made:

The alkali content is one of the most important factors for ASR. Hence, all parameters that influence the alkali content have to be considered carefully, especially if the influence is likely to change the relationship between the laboratory and the field. Thus, well established, but non-performance test methods should not be adopted carelessly, for example by boosting the alkali level.

For a performance test, similar ”alkali-conditions” (i.e. identical type and amount of cement, chemical admixtures and any external alkalis; insignificant alkali leaching etc.) should preferably be used as will be used in the field.

4 Properties of hydration products formed

4.1 Influence of storage conditions

For details, see Appendix 4.1.

An important property of hydration products related to ASR is their alkali binding capacity, because it has a strong influence on the composition of the pore solution and thereby on the alkali-silica reaction in concrete compositions. Storage conditions like the temperature as well as the time and the duration of different climate conditions have an impact on the alkali binding capacity of hydration products formed by different cement types or combinations of cements and supplementary cementing materials, SCMs. The temperature also controls the degree of hydration. As the quantity of reaction products increases, the quantity of alkalis that can be bound by them also increases.

In general, it is known that the propensity of the C-S-H phases to bind alkalis varies with their stoichiometric composition. The binding of alkalis to C-S-H phases increases with a decreasing Ca/Si ratio (Bhatty and Greening, 1978). C-S-H phases formed by pozzolanic reactions or the hydration of ggbfs have lower lime contents than their counterparts in Portland cement, and thus a higher alkali binding capacity. The amount of calcium in the hydration products of various fly ashes also has an effect on their alkali binding capacity. The higher the average Ca/Si ratio of the hydration products, the less alkali can they absorb (VDZ, 2009). Therefore, the efficiency of a given level of fly ash to mitigate a damaging ASR depends, among others, on its calcium content (Shehata and Thomas, 2000).

In addition to the influence of calcium, the average Ca/Si ratio of hydration products of fly ash (FA) increases with increasing storage time and increasing temperature, which results in a decreased alkali sorption capacity (VDZ, 2009). De Weert and Justnes (2008) have also documented that not only the C-S-H phases are changed when elevating the temperature from 20°C to 80°C, but also the aluminium containing phases. But more hydration products of fly ash are formed at 40°C and 60°C than at 8°C and 20°C, thus more alkalis can be bound (VDZ, 2009). So the temperature is affecting two opposing trends that influence the amount of bound alkalis; the amount of hydration products and their Ca/Si ratio. Apparently there is an optimum temperature for the highest alkali binding capacity when FA is present. Baetzner and Böhm (2009) found that the alkali concentration in the pore solution often was lowest at 40°C. The alkali binding capacity of hydration products of fly ashes is influenced by the availability of calcium and the degree of reaction of the fly ash (VDZ, 2009). The degree of reaction depends on the storage temperature. Therefore, it can be assumed that the alkali binding capacity will depend on the type of FA.

To access the alkali reactivity potential of specific concrete compositions in a relatively short time, mortar or concrete samples are often exposed to high temperatures at very early ages. Bokern (2008) assumes that an ASR takes place within 28 to 56 days in such accelerated laboratory conditions, when maximum alkalinity in the pore solution usually is achieved. Under normal conditions (20°C), the pozzolanic reaction of FA starts after the age of 28 days (Schäfer, 2004). If the concrete with FA is exposed to high temperatures at an early age, alkalis may be bound by the accelerated pozzolanic reaction that takes place before the ASR. This means that the pore solution has a lowered alkali hydroxide content when the ASR is about to start. To reduce this impact on the alkalinity of the pore solution, it is thus recommended to store the concrete samples under normal temperatures to allow a normal development of the pore solution composition. This is confirmed by Schmidt et al. (2009), where the accelerated concrete prism test at 60°C is extended by a pre-storage period of 28 and 90 days at 20°C before the samples are tested at 60°C.

As shown by Giebson et al. (2010b), higher temperatures during ASR tests will improve (densify) the micro-structure in concretes with SCMs (ggbfs in the particular study) compared to field conditions. Such a difference could result in an overestimation of the effectiveness of the used SCM in the ASR test. This has to be considered for an ASR performance test applicable for SCM-containing concretes, especially if external alkalis (slower ingress in a dense microstructure) play a role as in the cyclic climate chamber at the FIB. For the cyclic climate storage performed at FIB with an average storage temperature of 38°C, the reaction degree of the ggbfs used was found to be about 20% higher than for samples stored at 8°C. It was concluded that this difference cannot be neglected, but is probably low compared to other ASR test methods running at higher temperatures, for example the RILEM AAR-4.1 60°C (RILEM, 2006). To consider such effects, the testing period for SCM-containing concretes tested with the cyclic climate storage at the FIB is extended up to 16 cycles (12 months).

Up to 40% ggbfs, the Ca/Si ratio of the C-S-H phases and therefore also the sorption properties are similar to that of OPC (Schäfer, 2004). Higher temperatures may lead to higher degree of condensation of the silicate anions ($[SiO_4]^{4-}$ tetrahedra) in the C-S-H phases, and therefore to a lower Ca/Si ratio (Locher, 2005). Thus, the C-S-H phases formed can absorb more alkalis.

In summary, several authors have shown that high temperatures increase the rate of hydration and decrease the alkalinity of the pore solution, especially if applied to concrete compositions at young ages like in most ASR tests. The impact may be more pronounced if the concrete is made with cement with pozzolanic - or latent hydraulic materials (ggbfs) or combinations of cements and SCMs.

Another relevant question related to properties of hydration products, is how external alkalis influence the hydration products formed with OPC, ggbfs, FA and silica fume (SF). Several studies, e.g. Chatterji (1987), Kawamura (1988) and Sibbick and Page (1998), have shown that alkalis from external sources, e.g. NaCl from de-icing salts, increase expansion of mortar or concrete that contain reactive aggregates. According to Nixon et al. (1986), the introduction of sodium chloride to a cement paste, mortar or concrete at the mixing stage, results in an elevation of the hydroxyl ion concentration of the pore solution to a level similar to that produced by a Portland cement with an equivalent alkali level. This will increase the likelihood of a damaging ASR in concrete with alkali-reactive aggregates. According to Chatterji et al. (1986), free $Ca(OH)_2$ promotes Na^+ ions from the NaCl solution and OH^- ions from $Ca(OH)_2$, together with H_2O molecules to penetrate in a reactive grain. From Chatterji (2005), it can be derived that neutral alkali salts like NaCl may accelerate an ASR by increasing the ionic strength of the pore solution.

Information on the influence of external alkalis on the alkali binding capacity of the hydration products formed with OPC, ggbfs, FA and SF was not found.

4.2 Influence of aggregate type

The finest fractions of various aggregate types may be of significant relevance for the hydration products that form. This is due to the fact that very fine particles of certain rock types have the capability to react pozzolanic and hence increase the C-S-H phase, as suggested by Pedersen (2004). Examples of highly reactive materials being very effective pozzolans when crushed down to fines (finer than 63 microns) are Icelandic rhyolite and crushed bottle glass. These materials have a distinct amorphous silica phase. Fines from slowly reactive materials, such as Norwegian cataclasite and mylonite are not pozzolanic at normal curing temperatures, because the silica phase in these slowly reactive materials is well crystalline.

An important fact is that the pozzolanic behaviour of certain rock fillers, as described above, may mitigate the alkali-silica reaction, as discussed by Pedersen (2004) and Pedersen et al. (2004). It should be noticed that there are conflicting reports from the literature about the effect of particle size. A study by Diamond & Thaulow (1974) has shown that opaline aggregate even down to sizes between 20-30 microns are able to give harmful expansive reactions.

An important finding by Pedersen (2004) was a significant temperature effect. Some rock fillers not being pozzolanic at ordinary curing temperature may be highly pozzolanic at a temperature of 80°C. This fact is of high significance when using test regimes with very high temperature. Testing of mortar or concrete mixes with significant amounts of fines from alkali reactive rocks may then give a "false negative" result if tested at very high temperatures. This is due to the fact that the pozzolanic reactivity increases with increasing temperature. Pedersen (2004) examined exposure temperature of 20, 38 and 80°C, and concluded that methods using 80°C should not be used for performance testing of real mixes. The effect of exposure temperature of 60°C such as the RILEM AAR-4.1 CPT (RILEM, 2006) was not investigated in that study.

4.3 Influence of binder type

The relative proportions of the various compounds in Portland cement clinker affects the hydration products of cement paste. The hydration of C_3A, C_4AF and C_2S in cement are affected from the changes in the amounts of Ca^{2+} and OH^- in the pore solution. The presence of alkalis in portland cement also has an influence on the hydration of the individual phases. Ca/Si ratios[2] of C-S-H surrounding the clinker grains in ordinary Portland cement pastes generally range between 1.7 and 2.0 (Taylor, 1990). For neat cement pastes, the C/S ratio[2] is observed to be about 2.0 at the first day of cement hydration, while decrease to 1.4-1.6 several years after hydration. C-S-H has the ability to absorb Al^{3+}, Fe^{3+} and SO_4^{2-} ions from the surrounding pore solution (Ramachandran (editor), 1995).

Increasing the alkali level of cement clinker will lower the CaO concentration and increase the SiO_2 concentration of the pore solution (Taylor, 1990). Spierings and Stein (1976) found that the early hydration of pure C_3A is retarded by adding NaOH into solution, and the OH^- ion concentration in the solution is the determining factor. Addition of NaOH lowers the solubility of $Ca(OH)_2$ and increases that of $Al(OH)_3$.

Hou et al. (2004) conducted model experiments to simulate ASR formation in concrete and stated that the ASR and pozzolanic reactions are closely associated in concrete, except that the pozzolanic reaction proceeds before the formation of ASR gel. It was also concluded that both K and Na ions behave very similarly in the ASR reaction, but the rate of reaction is higher with K than with Na.

There are many similarities between pozzolanic reaction and ASR. The main difference is the particle size of the siliceous material. In contrast to rigid C-S-H, ASR product is quite deformable and sometimes mobile, it can imbibe water and swell. In the pozzolanic reaction, the alkali silicate gel is formed in a Ca^{+2} rich environment and it is quickly converted into C-S-H. In ASR, the environment is poor in Ca^{+2}, the cement paste cannot

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[2] Further in the report, the CaO/SiO_2 ratio is denoted Ca/Si ratio and C/S ratio interchangeably.

supply Ca^{+2} fast enough to prevent much of this gel from persisting for long periods (Taylor, 1990).

For blended cements, accelerating the pozzolanic reaction and ASR by exposing the concrete specimens too early to high temperatures may lead to misleading results (Bokern, 2008). High temperatures will activate the capacity of SCMs' alkali binding capacity, and the amount of $Ca(OH)_2$ in the system is reduced. Correspondingly, at high temperatures, the pore structure at early stage is altered, the capillary pores are decresed and the transport of alkali and water to the reaction sites are hindered. This phenomena is also related to the rate of the reaction or the reactivity of the aggregates.

Duchesne and Berube (1995) studied the composition of cement hydration products of blended cements containing silica fume, fly ash and slag, respectively. The pore water solution extraction and EPMA were applied to the concretes cured in 38°C and 100% relative humidity for three years. The mean CaO/SiO_2 of the portland cement samples was 2.05, while this value ranged between 1.24 – 1.46 for blended cements independent of the type of the SCM. The pore solution alkalinity of all of the blended cements revealed a decrease, except for a very high alkali fly ash. It was concluded that the reduction of pH of the pore solution and the reduction of expansions is mainly attributed to the incorporation of alkalis by the low C/S hydration products in the presence of SCMs. The effect of ggbfs is somewhat different as will be discussed later.

It was shown by Diamond (1997) that if NaOH is dissolved in the mix water prior to the addition of cement (i.e. alkali boosting), Na^+ ion concentrations increase, but measured OH^- ion concentration was less than expected. Conversely, the increased Na^+ ions in the pore solution are balanced with an immediate boost in the concentration of SO_4^- ions rather than OH^- ions (see also chapter 3.4). This is due to an immediate reaction between NaOH and gypsum of cement. A consequence of such an early increase of SO_4^- ions in the pore solution might be delayed ettringite formation (Diamond and Ong, 1994). The C_3A content of cement is also important for this issue.

In blended cements, C-S-H appears to be less crystalline and lower in calcium than in portland cements. The difference is mostly observed in silica fume blends, where an apparently amorphous C-S-H constitutes a homogeneous paste with strong interfaces between solid particles and matrix (Regourd, 1987). Huang and Feldman (1985) found that silica fume accelerates both C_3S and C_3A hydration in the first few hours. Silica fume reacts with the $Ca(OH)_2$ formed during hydration within 28 days. Depending on its inclusion level, silica fume incorporation decreases the Na^+, K^+ and OH^- ion concentrations in the pore solutions, while increases the Na^+ and K^+ content of C-S-H.

The partial replacement of 10% portland cement with silica fume was reported (Duchesne and Berube, 1995) to significantly increase the alkali content of hydrates. Durand et al. (1990) found that the Ca/Si ratio was found to be 1.70 for a cement containing 25% ggbfs and 1.43 for a cement with 5% silica fume. The alkali binding capacity of the hydrates increases as the Ca/Si ratio is decreased, and the removal of alkalis from the solution increases with time, more alkalis were removed from the solution of higher alkalinity. If high Ca/Si ratio hydrates are present in high alkalinity pore solution, Ca^{2+} ion from the hydrates may exchange with alkali cations of the reacting solution. This would result in a significant increase in the alkalis retained by the solids. However, these alkalis are released into the reacting solution at later ages (Bhatty and Greening, 1978). Tenoutasse and Marion (1987) stated that silica fume forms microcrystalline hydrosilicates containing alkalis similar to alkali-silica gels. The expansion property of this product is related to its potassium content. This product does not produce expansion, because it occupies the available space in the paste and forms when cement is still plastic.

Data available from field studies from concrete structures and experimental laboratory studies related to the use of fly ashes from bituminous coal sources both show the efficiency of low calcium (i.e. <10% CaO) fly ashes in decreasing the ASR expansions. However, high calcium fly ashes are not as effective, and may even reveal higher expansion values in the laboratory when compared to control samples without fly ash; Dunstan (1981) and Shehata et al. (1999). In an extensive study investigating the effect of several types of fly ashes from North America in various amounts by using concrete and mortar bar expansions tests, Shehata and Thomas (2000) concluded that the minimum level of replacement required to control expansion to 0.04% at 2 years (38ºC CPT) generally increased as the calcium or alkali content of the fly ash increased or as its silica content decreased (see 3.4). The fly ashes that were found to be most effective in reducing the alkalinity of the pore solution expressed from paste samples were also found to be the best for controlling ASR expansion (Shehata et al., 1999). Sibbick and Page (1995) stated that the effectiveness of the PFA's in suppressing ASR was dependent on the initial alkali content of the mix and on the alkali content of the PFA, but the results of pore solution analysis did not provide a simple explanation for the corresponding expansion data showing that the differences in expansions cannot only be explained by the changes in the pore solution chemistry. Regourd (1987) stated that the C-S-H formed after the pozzolanic reaction of fly ash is apparently more amorphous than the C-S-H from ordinary portland cement, it also contains more Al, with Ca/Si ratio between 1.0 and 1.50. Duchesne and Berube (1994) concluded that the addition of fly ash resulted in hydrates that contain effectively much more alkalis than ordinary portland cement hydrates. As a result, a higher proportion of the total amount of alkalis released by the cementitious materials are entrapped in the hydrates.

The composition and morphology of hydration products of slag(ggbfs)-incorporating cementitious systems are quite similar to that of neat Portland cement hydration products; the main differences being the decreased amount of CH in the hydrated slag cements and decreased Ca/Si ratios ranging between 1.55-1.79. For any specified drying condition, the calculated water content of slag cements are lower and the porosities higher than those of pure Portland cement pastes, and this appears to be true in varying degrees of composite cements in general (Taylor, 1990). Duchesne and Berube (1995) concluded that the hydrates formed in the presence of 50% slag do not contain significantly more alkalis than ordinary portland cement hydrates, nor do they entrap a much higher proportion of the alkalis released by the cementitious materials. Alkali activated slag cement concrete was found to be more susceptible to ASR when compared with other types of cements, due to abundant supply of alkalis (Bakharev et al., 2001).

Rice husk ash is produced by burning the rice husks at 350-600^{o}C, and the ground material becomes quite pozzolanic (similar to microsilica), because it contains amorphous silica and has a high surface area. The pozzolanic reaction depletes the CH content of pastes to about 1% at 28 days, and the hydration product C-S-H has Ca/Si ratio of about 1.3 (Khan et al., 1985).

Zeolites are found to be effective in reducing the alkali aggregate reactions. Naiqian and Tingyu (1998) explain this behaviour as the decrease of pore solution alkalinity in concrete through ion exchange and pozzolanic reaction. The effectiveness of this natural pozzolan depends on its fineness and amount; Naiqian and Tingyu (1998), Andiç-Çakır et al. (2008).

Incorporation of lithium salts in order to suppress ASR expansion is a common procedure; chemical admixtures are added into concrete to prevent ASR. Lithium salt incorporation may increase the expansion when used less than the necessary dosage due to their effect on increasing the OH^- concentration in the pore solution (Diamond and Ong, 1992; Stark et al., 1993). Diamond (1999) stated that $LiNO_3$ is an exception, which does not show such a pessimum effect. Feng et al. (2005) summarized the findings in the literature about the effect of lithium salts on the reaction products formed, and stated that the efficiency of lithium salts in suppressing the ASR expansions depend on the nature and reactivity of the aggregate, the form of lithium, the amount of alkalis in the pore solution and the dosage of lithium salt added (lithium to alkali molar ratio). The effect of lithium on silica dissolubility is not clear, yet different types of lithium salts may show different effect. The mechanism of the effect of lithium salt on ASR expansions will be discussed further in chapter 6.5.

It is of importance to know if there are other side effects while using lithium salts as a chemical admixture for concrete. It is known that there is no adverse effect of lithium incorporation to the workability and compressive strength development of concrete (Andiç-Çakır and Yüksel, 2009), while there are some effects on setting time of fresh concrete. Modrý (2004) obtained that Li_2CO_3 and $LiOH.H_2O$ accelerated the hydration of cement, while $LiNO_3$ only had a slight acceleration effect. Andiç-Çakir and Yüksel (2009) found that the setting time of the specimens incorporating Li_2CO_3 and $LiNO_3$ were quite similar to that of control specimens without lithium salt. However, LiF addition delayed the setting time substantially.

To <u>sum up</u>; Some test methods that use an elevated temperature may give misleading results for blended cement containing samples. High temperatures will activate the alkali binding capacity of SCMs and, especially at early stage, the pore structure and corresponding mass transport mechanism of the concrete are altered. Furthermore, alkali boosting during testing may increase the sulphate ions in the pore solution in which some researchers claim will increase the risk of delayed ettringite formation. It should also be noted that different types of SCMs might show different effects on the properties of the reaction products formed, mainly on the Ca/Si ratio of C-S-H. More documentation is needed to correlate the field vs. laboratory performance of lithium-incorporating concrete.

4.4 Influence of mix design / casting

The possible influence of the composition of the concrete mix and how the concrete samples are cast and cured are discussed more in detail in *Appendix 4.4*. In this sub-chapter, a summary is given.

The <u>water/binder ratio</u> in particular when using a CEM I cement, is a very important factor for the properties of the hydration products formed (Chindaprasirt et al., 2008). If too little water is added to the concrete mix, other reaction products may be formed. However, for a normal concrete composition, i.e. water/binder ratio in the range 0.4 to 0.5, the hydration products will not be much different. It might be possible that the Ca/Si ratio in the C-S-H phases (from C-S-H I with Ca/Si ratio 0.8 to C-S-H II with Ca/Si ratio 1.5) is varied by changing the water/binder ratio. Nevertheless, the reaction kinetics of the hydration reactions and the obtained structure of the material (concrete) may change. The change of water/binder ratio also implicates a different alkali concentration (by extraction), which leads to a different behaviour and may result chemically in other reaction products or a different physio-mechanical behaviour of the product.

<u>Boosting the alkali level</u> by addition of alkalis to the mixture will have an effect on the hydration products, as reported by Kagimoto et al. (2004), Bérubé and Tremblay (2004) and Pacheco-Torgal et al. (2008). For example, if the alkali concentration is increased, this will have an effect on the ettringite formed by influencing e.g. its stability and shape (Tenoutasse and Ghodsy, 1992; Cody et al., 2004). This will change the hydration kinetics, as the hydrated structures are formed during the reaction. This effect may take place for the other cementing materials.

Böhm and Baetzner (2008) showed that boosting a concrete with alkalis is not equivalent to a “natural” alkali content. Leemann and Lothenbach (2008a; 2008b) also questioned the Na_2O equivalent concept, i.e. the relation between sodium and potassium. However, even new de-icers, potassium or sodium acetates, used for highways or air field pavements may generate ASR (Stark and Giebson, 2008).

It’s well known that the temperature during curing influences the reaction kinetics and indirectly the hydration products. All hydration products, by definition, are also influenced by the curing humidity and time (Hewlett, 1988).

The chemical admixture type may also be a very important parameter. Mostly the admixtures influence the behavior of the material in a non-solid state, like for example fluidity and the need for water to be workable (Low Norman, 1980). They may, however, also have an effect on the hydration products that are formed, due to reaction kinetics, adsorption of the admixture molecules on surfaces of hydrated (or at that moment still not reacted) cement particles (Ismail and El-Hemaly, 1991; Jun-zhe et al., 2004; Silva and Monteiro, 2006; Chindaprasirt et al., 2008).

Air entrainment addition might be effective in decreasing the expansion due to ASR; Jensen et al. (1984) and Hobbs (1988). The effect is rather mechanic; air entraining agents provide escape boundaries for ASR gel. Boyd et al. (2000) stated that the addition of a lightweight aggregate may show a similar behaviour. The same may be assumed to be the consequence if prisms for ASR testing are poorly compacted.

Hagelia (2004) has experienced the effect of air voids in a real structure in Norway, some segments of the retaining walls were cracked and some not. Micro-structural analysis showed that the non-cracked cores were air entrained and the cracked cores were non air entrained. However, there were also discovered some slights differences in the concrete composition, as well. Recently, Fournier et al. (2009) concluded that air-entrainment does not have a clear effect on ASR expansions of exposure blocks stored on Texas outdoor exposure site. Neither did FIB get any positive effect on ASR by increasing the concrete air content – see chapter 3.5.

The retarder addition to mixtures containing air-entraining admixture produces further reductions in expansions. The action of the retarder might be attributed to the changes in the availability of lime and alkali, production of lower C/S ratio phase and delay in the formation of a rigid structure of the paste (Gillot and Wang, 1993; Ramachandran, 1998).

The form oil, the admixture type and the curing conditions, dry chamber (65% relative humidity and 20°C) or wet chamber (>95% relative humidity and 20°C), will normally not change the properties of the hydration products formed, but will influence the superficial properties, respectively, by the formation of a hydrophobic film, another matrix composition and carbonation.

To sum up; Irrespective of the type of curing, it was stated that changing the water/ cement ratio will also change the Ca/Si ratio of C-S-H phases. Boosting the alkali level may alter the ettringite formed, and the reaction kinetics will change. It is also considered that all hydration products (and rate of their formation) are influenced by the humidity of curing and the curing period. There are contradictory findings in the literature about the effect of air-entrainment on ASR expansions; however, the effect seems to be mechanical rather than chemical.

5 Aggregate reactivity

For details, see Appendix 5.

5.1 Influence of storage conditions

Some parameters related to storage conditions seem to be of highest interest concerning the occurrence of ASR and the amount of reaction product formed, which will contribute to expansion of mortar and concrete. Regarding these parameters, temperature of exposure and the existence of humidity and alkalis in the system should be highlighted. Numerous findings are presented in the literature about these and other parameters regarding their influence on the process of ASR, see e.g. Fournier et al. (1991), Fournier and Bérubé (1991), Fournier et al. (2004) and Ben Haha et al. (2007).

Experiments show that the exposure temperature influences the aggregate reactivity. The solubility of SiO_2 increases with the temperature, Iler (1979). However, the temperature should not be analysed in isolation, as it works simultaneously with other factors, e.g. the composition of the concrete pore solution as discussed in chapter 3.4. In general, high temperature can induce higher rates of reaction, a greater amount of gel is formed and higher expansion is observed at a given time.

High exposure temperature also seems to activate “non-reactive” aggregates (Shayan et al., 2008). Some laboratory tests show opposite results, with lower ultimate expansion at higher temperature for similar specimens – see e.g. Fournier et al. (2004). The authors explain this phenomenon referring to more alkali leaching and changes in the pore solution composition when elevating the storage temperature (see chapter 3.4).

Fournier et al. (2008) performed field tests on concrete blocks in two different locations, one in Texas and one in Canada, to study the effect of temperature. They concluded that the expansion is faster and higher for the place with highest exposure temperature, but it depends on the type of aggregate selected. The difference in expansion increases with decreasing reactivity level.

For reactive aggregates, laboratory tests show that expansion increases with increasing duration of the test (Fournier et al., 1991; Kuroda et al., 2000). The behaviour is different when comparing sedimentary aggregates with igneous and metamorphic rocks, meaning that the aggregates react in a different way. Time has no effect for completely non-reactive aggregates (Fournier et al., 1991; De Grosbois and Fontaine, 2000). However, some very slowly / marginal reactive aggregates may expand beyond the critical limits after a long time of exposure (Lindgård et al., 2010). With time, a larger amount of ASR gel is produced (Kawamura et al., 1998; Kuroda et al., 2000).

Many references are found concerning the expansion of prisms of various sizes, but these have seldom been related to aggregate reactivity. According to Bakker (1983), large prisms expand slower to begin with, but they continue to expand at a steady rate. When testing extremely reactive aggregates, smaller specimens expand more, even though the extent of alkali leaching is higher for smaller prisms (see chapter 3.2). This fact leads to the conclusion that there is an influence of prism size on expansion, which is assumed to be related to the aggregate reactivity combined with the aggregate particle size.

Internal moisture and alkali content in the concrete or mortar mix are important factors affecting the reactivity of aggregate, and they are both necessary for the reaction to take place (these parameters are also further discussed in chapter 2 and 3, respectively).

One of the premises for ASR to happen is that enough water should be available for reaction (Bérubé and Fournier, 1993). There is thus an influence of the amount of water present in the exposed specimens on the measured expansion.

The storage parameters; type of container, water level and submersion of specimens should be studied together as they interfere with each other. Most of the experiments performed deal with type of container, wrapping (or not) and storage above water or submerged (see also chapter 2).

No direct references were found connecting the external humidity to the reactivity of aggregates, as it seems to influence in a higher degree the rate of reaction and the amount of products formed, resulting in increased expansion.

The presence of alkalis influences the reactivity of aggregates and the extent of the reaction. Therefore, for a specific aggregate, more alkalis available means more expansion, due to a higher concentration of OH^- in the concrete pore solution. Fournier et al. (2004) have shown that non-reactive sands can have components which are activated by high alkali content. Also Rivard et al. (2007) and Böhm and Baetzner (2008) studied the effect of the alkalinity of pore solution on ASR.

There are a large number of papers concerning the quantity of alkalis added to the mortar or concrete mix (Rogers, 1990; Shayan, 1992; Fournier et al., 2006; Lu et al., 2006d; Rivard et al., 2007; Bokern, 2008; Shayan et al., 2008). For a specific test, it is verified that the result for the same aggregate may run from "innocuous" to "reactive" depending on the content of alkalis available for reaction.

The content of alkalis used in laboratory testing of aggregates is normally higher than that applied in field concretes, as standards regarding the avoidance of ASR state an upper limit for weight percentage of alkalis allowed or, alternatively a maximum content of alkalis in kg/m^3 allowed. In this respect, some of the laboratory tests are much more severe than field conditions, meaning that the evaluation of reactivity is performed on the "safe" side, or for the worst conditions admitted.

When alkalis are added to the immersion solution, the influence of the cement alkali content on mortar bar expansion significantly decreases due to ingress of alkalis into the concrete. It has been verified that different aggregates react in a different way when exposed to salt solutions, and also that the reaction is dependent on the type and concentration of the salt used (NaOH, NaCl, KOH, LiOH or just moisture). Lawrence and Vivian (1961), Kuroda et al. (2000) and Lu et al. (2006c) also found that the expansion increased and then decreased, concluding that there was a "pessimum" effect for amount external alkalis added.

Among the parameters listed in this chapter, only a few or no references were found for the following issues:

- Temperature during curing of specimens (of mortar of concrete), which it has been suggested is not relevant for the occurrence of ASR (Fournier and Bérubé, 1991).
- Temperature when measuring the specimens, which depends on the type of test performed (i.e. are the samples cooled before measuring, or not?).

To sum up: Experiments show that the exposure temperature influences the aggregate reactivity. The solubility of SiO_2 increases with the temperature, a greater amount of gel is formed and higher expansion is observed at a given time since the reaction rate is accelerated by temperature. Nevertheless, normally lower ultimate expansion is obtained at higher temperature for similar specimens - see e.g. Fournier et al. (2004). This is assumed to be due to more alkali leaching (see chapter 3.2) and changes in the pore solution composition when elevating the storage temperature (see chapter 3.4). Thus, the temperature should not be analysed in isolation, as it works simultaneously with other factors. High exposure temperature also seems to activate “non-reactive” aggregates (Shayan et al., 2008).

Fournier et al. (2008) performed field tests on concrete blocks in two different locations, one in Texas and one in Canada, to study the effect of temperature. They concluded that the expansion is faster and higher for the place with highest exposure temperature, but it depends on the type of aggregate selected. The difference in expansion increases with decreasing reactivity level.

The presence of alkalis has an influence on the reactivity of aggregates and on the extent of the reaction. Therefore, for a specific aggregate, more alkalis available mean more expansion, due to a higher concentration of OH^- in the concrete pore solution. For a specific test, it is verified that the result for the same aggregate may run from “innocuous” to “reactive” depending on the content of alkalis available for reaction.

It has been verified that different aggregates react in a different way when exposed to salt solutions, and also that the reaction is dependent of the type and concentration of the salt used (e.g. NaOH, NaCl, KOH or LiOH).

5.2 Influence of aggregate type

Features associated with ASR are different for fine and coarse particles of a specific aggregate type. Some aggregates show higher expansion for larger particles, some for intermediate sized particles, and sometimes small particles have stronger reactivity. Concerning the aggregates with pessimum content, more reactive aggregates show maximum expansion for lower contents of reactive silica (Shayan, 1992; Bektas et al., 2004).

For slowly reactive aggregates such as some granites, the use of very fine aggregates can destroy the original microstructure characteristic of the rocks (Lu et al., 2006a), under-estimating the alkali reactivity of the rocks in the accelerated tests (e.g. size used in AMBT and Chinese autoclave method). These tests fail to identify the reactivity of some slowly reactive aggregates, compared to field performance.

According to (Wigum and Lindgård, 2008), slowly reactive Norwegian coarse aggregates have proven to be more harmful in field than fine aggregates. This has been accounted for in the Norwegian regulations (Norwegian Concrete Association, 2004) by differentiating the critical limits in the Petrographic method and the accelerated mortar bar test (Norwegian Concrete Association, 2005).

For rapidly reactive aggregates, the opinions are contradictory (Vivian, 1951; Zhang et al., 1999; Ramyar et al., 2005; Lu et al., 2006b; Multon et al., 2008):

- The larger the size of the aggregate particles, the higher the expansion (e.g. siliceous limestone in AMBT); larger particles lead to smaller expansion at early ages, but increase continuously at later ages.
- Larger expansion occurs for medium sized or smaller sized particles.

For aggregates showing pessimum behaviour such as opal aggregates, Diamond and Thaulow (1974) concluded that the smaller fractions expanded faster than the coarser material, which needed a prolonged exposure, but the total expansions were of the same order. The authors also concluded that the expansion occurs suddenly and is complete in a relative short time with fine reactive particles, while with larger sizes the expansion is slower and more gradual.

The classification as slowly reactive, rapidly reactive and non-reactive aggregates should be based on field performance, which is not always possible. However, it is known that, in particular for slowly reactive aggregates, the accelerated mortar bar test may give false results of non-reactivity. The reverse may happen with non-reactive aggregates, which may be classified as reactive because the conditions in the test are too severe for some types of aggregate (Bérubé and Fournier, 1993).

The classification of non-reactivity is not universal. Tests performed with different "non-reactive" natural sands mixed with a specific reactive aggregate show different results depending on the test method applied and the laboratory conducting the test (Ideker et al., 2006; Shayan, 2008).

Increased permeability in aggregates with higher porosity may enhance the alkali reactivity, due to easier access to concrete pore fluids (Broekmans, 2002).

A main challenge today regarding identification of aggregate reactivity is to find an accelerated test that can correctly classify aggregates, in particular those considered non-reactive or slowly reactive. It is strongly recommended that all aggregates are classified by petrography before a performance test is executed (Bérubé and Fournier, 1993; Sims and Nixon, 2006).

The shape of the particles may also be of importance. Ramyar et al. (2005) found that the angularity of the particles has negligible effect on ASR expansion for very large and very small particles. However, for intermediate fractions, the angularity effect on ASR is more evident, and the effect of size of the particles is more pronounced in crushed aggregate.

To sum up: Features associated with ASR are different for fine and coarse particles of a specific aggregate. Some aggregate types show higher expansion for larger particles, some for intermediate sized particles, and sometimes small particles produce the most expansion.

Concerning the aggregates that exhibit pessimum behaviour, more reactive aggregates show maximum expansion for lower contents of reactive silica (Shayan, 1992; Bektas et al., 2004). The proportion applied during laboratory testing is thus of great importance.

The classification of non-reactivity is not universal. Tests performed with different "non-reactive" natural sands mixed with a specific reactive aggregate show different results depending on the test method applied and the laboratory conducting the test (see also chapter 3.3).

A main challenge today regarding identification of aggregate reactivity is to find an accelerated test that can correctly classify aggregates, in particular those considered non-reactive or slowly reactive. It is strongly recommended that all aggregates are classified by petrography before a performance test is executed.

5.3 Influence of binder type

The major discussion on effects of the binder type is covered in chapter 4 and partly in chapter 3. However, some aspects of the aggregate/binder interaction are not explicitly dealt with in the literature, but still deserve some attention. Although indirectly covered by extensive testing of various types of aggregate with different binders in a range of testing methods, the joint and simultaneous action of these components was not, as such, sufficiently covered. This may also partly reflect the fact that different and partly contrasting measures have been adopted and coexist regionally.

Bokern and Siebel (2004) report discrepancies between laboratory testing and outdoor storage conditions for SCM containing concrete. This is in contrast to the previously (chapter 3.4) referred report by Thomas et al. (1995). Also, the traditional concrete expansion tests to a poor extent are able to distinguish pessimum effects, unless indirectly by investigating a series of various material proportion ratios. There are several more or less complex mechanisms that may explain this, but – again – in the present context we will try to elaborate another one:

The ASR deterioration mechanisms include, amongst other factors, ion diffusion, crystal dissolution, chemical reaction and physical actions. All these mechanisms are sensitive to temperature and pH level conditions. The kinetics are different for cement clinkers, SCMs, various aggregate minerals and “mutually dependent reaction products”. Most probably, the *change* in kinetics with change in temperature, pH, moisture conditions etc. lead to a time shift in the reaction process, possibly influencing reaction mitigation needs or effects: One combination working under one (temperature) may not work under another, which is why a strong experience base for the correlation between field and laboratory conditions still has to be established.

Testing at 60°C, more siliceous material from the aggregate is likely to be dissolved, compared to that at 38°C or at ambient conditions, since the solubility of SiO_2 increases with the temperature (Iler, 1979). This may require a higher rate of SCM reaction, lower C/S ratio (Malhotra et al., 1993) or other property changes to cope with the increased “demand”. Alternatively, increasing the temperature promotes the pozzolanic action of the SCM, but also the early hydration of the cement clinker.

To sum up; It is likely that a rapidly reacting aggregate, being further “accelerated” in a test, apparently will require another (stricter) degree of “measure” than a more slowly reacting one. To avoid development of ASR when testing a rapidly reactive aggregate type, the alkali content in the pore water must be lowered already in the early phase of the testing period. This is also compatible to the reported advantages of slag (ggbfs) and particularly fly ash with high reactivity (e.g. fineness) with respect to required dosage and aggregate reactivity (Thomas et al., 1997).

5.4 Influence of mix design / casting

Assumed covered elsewhere in the report.

6 Reaction product formed during the exposure

6.1 Influence of storage conditions

For details, see Appendix 6.1A and 6.1B

Moranville-Regourd (1989) reported that the alkali-silica reaction products observed in concretes or mortars that have been cured in accelerated conditions are quite similar to those found in cores taken from structures; however, other workers have observed differences due to storage conditions as discussed below.

Regarding the influence of storage conditions with respect to ASR reaction products formed, there are some findings present in the literature that highlight the expansion as a function of the composition of the gel, which is also related to a number of factors of storage conditions, e.g. temperature, humidity, boosting of alkalis. A great number of experiments have been performed with varied exposure temperature for similar specimens, but with other variable test conditions, simultaneously; Fournier et al. (1991), Grattan-Bellew (1997) and Ben Haha et al. (2007). In general, high temperature can induce higher rate of reaction, thus a greater amount of gel is formed and an increased expansion is observed at early ages (Fournier et al., 1991). It is also observed that higher temperature results in a greater amount of Ca in the gel, assumed by some as a prerequisite for the formation of expansive gel (Kawamura et al., 1998).

Gavrilenko et al. (2007) compared concrete cores taken from Spanish dams and mortar bars made up with the same aggregates (crushed granitic mylonite and quartzite) and tested according to the ASTM C-1260 testing procedure (water/cement ratio 0.47; bars 25.4·25.4·287 mm^3 cured 24 h in a wet chamber at 20°C and then at 80°C for 24 hours; the bars are then submerged in a 1N NaOH solution at 80°C for 14 and 28 days). As an exception, they performed the test method by using less cement (400 g) than specified in the testing procedure and extended the expansion recording period up to 49 days. Alternatively, they have evaluated the effect of drying, by drying the specimens at room temperature, at 48ºC for 15 days and at 90ºC for 2 days, respectively. After testing, mortar bars and concrete cores were both studied by scanning electron microscopy and semi-quantitative analysis of gels were performed by EDX on specimens in natural state (no polishing). In both cases they found large varieties of gel: compact smooth gel (amorphous), lepispheres and sheet sponge or clot morphology (crystalline/porous). Even if this accelerated testing procedure does not seem to give rise to specific reaction product morphologies, they found a very different chemical composition between field and laboratory reaction products. Gels formed in mortars (alkali-boosted) were highly enriched in Na and poor in Ca, with often more silica than in the field concretes. They also observed that the drying conditions in the testing procedure do not influence the morphology and the chemical composition of the gel precipitated. The authors emphasize that in accelerated test conditions like 80ºC temperature and unlimited alkali boosting, very high expansion values are obtained due to the change in the reaction chemistry by the addition of external alkalis to the pore solution. However, in real concrete structures, alkalis present in pore solution may be precipitated in the gel before excessive silica dissolution takes place and consequently, the reaction rate decreases.

Regarding other properties of ASR gel, it was found that products obtained in laboratory tests are similar to those identified in field concretes (amorphous and crystalline). This fact is important as it means that temperature is probably not as important to the morphology of the alkali-silica gel as it is for the reactivity, rate and amount of gel produced (Fournier et al., 1991).

In the late 80's, Davies and Oberholster (1988) compared alkali-silica products formed in field concretes with those formed during the 80°C NBRI test (Davies and Oberholster, 1987). They showed that, compared to the field, the NBRI test accelerates the reaction, but does not modify the naturally occurring process. Nevertheless, during the test they noticed fluid gels exuding into the NaOH solution, in the form of thin filaments. SEM examinations of gel conducted at the completion of such accelerated laboratory tests have revealed that morphologies were very similar to those found in field concretes (Peterson et al., 2006) irrespective of whether NaOH or KOH solutions were used (massive gels, sponge-like texture and rosette-like phase). By washing gels with distilled water, both authors observed drastically reduced gel alkali content and Ca/Si ratio. They have drawn from this result that alkali ions present in the gels are likely absorbed rather than chemically bound.

In 2003, Zidzislawa compared alkali-silica reaction products formed during a conventional test (long test duration) and an accelerated test. The author started with 25x25x285 mm^3 mortar bars, with w/c of 0.47, but used cement alkali-boosted with K_2SO_4 instead of NaOH in order to get alkali contents from 0.35 to 1.10% Na_2O_{eq} of the cement. Half of the bars were stored at 38°C and 95% RH, while the other half was immersed after curing into a 1N NaOH solution at 80°C (NBRI testing procedure). For the latter, expansion measurements were taken every second day, over a period of 14 days. The researcher chose K_2SO_4 to get more realistic pore solution, knowing that most cements contain more potassium than sodium. SEM observations of mortar stored for 30 months at 38°C or 14 days in 1N NaOH solution at 80°C showed the same ASR-gel morphology, but large quantities of massive ettringite were found in cracks, around some aggregates and in air voids only for the first set of prisms. No ettringite was found in the second case (not stable > 65°C). According to this author, this secondary ettringite formation can play a considerable role on expansion, hence higher expansion was found with the 38°C storage than with the accelerated testing (around 0.65% versus 0.11%). He assessed, too, that addition of potassium in the sodium-potassium silicate gel increased its viscosity and swelling properties. On the other hand, he derived from his own test results that alkali content in cement considerably affects linear changes in the accelerated expansion test.

Gavrilenko et al. (2007) similarly observed ettringite acicular crystals in real concretes drilled from dams, while only minimal quantities of ettringite were observed at the mortar bar samples cured in 80°C and 1N NaOH solution, which was present close to the gel surface. Conversely, Gavrilenko et al. (2007) stated that the gels containing Na_2O are more expansive than gels containing K_2O, while supporting the double layer theory by Powers and Steinour (1995). The theories present in the literature about the effect of different alkali metal ions on the expansion of ASR gel are explained in detail in chapter 6.4.

Nevertheless, Kawamura and Iwahori (2004) saw that pressure exercised under restraint is higher with Ca-rich gel than with alkali-rich gel (this restraint being minimised in thin mortar bars). In field concretes, alkali content is often limited, while calcium is continuously brought into the pore solution due to portlandite dissolution. So in the field, ASR-related expansion can be more intense. In laboratory mortar bars, the high level of sodium content (resulting from the NaOH enrichment of the mixing water or storage in alkaline solution) leads to increasingly sodium-rich gel and probably artificially raises the silica-dissolution rate of some aggregates.

When stored under humid conditions and at elevated temperature, the water uptake of the reaction products is accelerated. The fluidity of the gel is also increased, so that the gel may flow into the surrounding porous structure without creating any damage. This might be more effective in the presence of a porous aggregate. In the presence of SCMs, due to the lower availability of $Ca(OH)_2$, the characteristic reaction rim preventing the gel penetrating into the surrounding paste is less solid (Bokern, 2008).

One measure to avoid the discrepancies between laboratory specimens and field conditions is altering the curing regime before exposure to accelerated conditions. While testing the effectiveness of SCMs, 28 or 56 days of curing at ambient temperature may help the concrete to achieve the maximum pore solution alkalinity level. However, even after this pre-curing period, the fluidity of the gel may still be a problem at high temperatures (Bokern, 2008). Accelerating the curing conditions by submerging the specimens in alkali solutions at high temperatures will also lead to increased alkali levels of ASR products (Andiç-Çakır and Çopuroğlu, 2009).

Kawamura and Iwahori (2004) also pointed out that the viscosity of low Na_2O/SiO_2 gels is much higher than high Na_2O/SiO_2 gel. Thus, viscosity of alkali-rich gels in mortars may be so low that they could not exhibit high expansive pressure. This low viscosity leads to exudation of great amounts of gel on the surface of bars with alkali content higher than 2% of the cement. This exudation limits the gel content inside the mortar bars and possibly resulting in reduced expansion.

Struble and Diamond (1981) measured swelling properties of alkali silica gels of various Na_2O/SiO_2 ratios. Under "free-swelling conditions" they recorded swelling ranging from 0.1 MPa to almost 11 MPa. Gels with Na_2O/SiO_2 ratio of 0.33 and less exhibited the lowest swelling pressures. They found that the presence of calcium in the gel did not noticeably reduce either its swelling or its pressure-developing ability.

With extended exposure time, a larger amount of ASR gel is produced, leading to a higher expansion (Gavrilenko et al., 2007). There is no direct indication to the correlation between time and the properties of gel. However, it is known that the composition of gel evolves with time; initially the gel absorbs lots of water, but does not exert significant pressure. In later stages, due to the evolution of the reactions, the Ca content increases and the gel becomes more viscous and expansive than the original alkali-rich gel. The Ca content is also a function of the place where gel occurs inside the concrete; Knudsen and Thaulow (1975), Kawamura et al. (1998), Fernandes (2009). Among others, Bokern (2008) has shown that increase in the alkali content in ASR gel in mortars decreases the expansion. He also showed that the addition of SCM's may hinder deleterious ASR in laboratory tests, but not always in the field, partly because the viscosity of the gel decreases at elevated temperature and at a higher RH level.

The alkali-silica reaction product has initially low fluidity and considerable swelling capacity in the presence of water. There is also evidence – at least under laboratory conditions - that dehydrated gel can be rehydrated and will re-expand when additional water is added to the specimen (Larive et al., 2000). However, dried and carbonated gels are unlikely to regain their expansive properties, and they are not soluble in water (Poole, 1992). Continuous cycles of wetting and drying of concrete will lead to localised alkali concentrations in the pore solution. This alkali concentrated regions are generally located in the outermost regions of concrete structures after drying of concrete. Thus, even for concrete containing low alkali cement, local ASR formation might become possible (Farny and Kosmatka, 1997).

It has been observed that the quantity of gel produced is much reduced when there is no external water supply, and also that higher humidity leads to higher expansion (Larive et al., 2000).

The questions about type of container / wrapping or no-wrapping seem to influence more the amount of gel, than the properties of gel. In the literature, expansion is usually connected to the amount of gel and not to the composition, when referring to storage conditions. However, it should be clarified in what extent the existence of alkali leaching can influence the composition of gel, regarding the content of Ca and alkalis.

Regarding the size of the prisms, exudation of gel from smaller prisms is more likely when compared to larger prisms. In real structures, exudations are composed of alkali-silica gel with no Ca (Fernandes, 2009). *This issue should be investigated in order to compare the composition of gel inside smaller and larger prisms with field concrete (large cross-section) by using petrographic methods and SEM.*

To sum up, the most important storage conditions seem to be temperature and humidity, since these factors affect the pore solution chemistry as well as the rate of formation and expansion properties of ASR products, even though the morphology of the ASR-gel seems to be the same in laboratory specimens and in field concrete. Other important issues to consider are whether alkali boosting is applied or not in the testing procedure and the type of alkali compound used (contradictory findings for alkali boosting), since these two factors seems to alter the swelling properties of ASR products. Availability of restraint, size of test prisms and application of any wrapping seem to have secondary effects on gel properties.

6.2 Influence of aggregate type on ASR products formed

For details, see Appendix 6.2

In laboratory tests and field concrete, it is observed by petrography that fine reactive particles show different behaviour from coarse reactive particles (Fernandes, 2010). It is usual to find larger particles with cracks extending to the cement paste and partial substitution by gel in rims and along the interstices between quartz grains. In small reactive particles, gel usually substitutes at a higher rate the silica in the grain, but without visible expansion. These features can be concomitant, showing the direct influence of size in the reactivity of aggregates.

The literature review reveals that different tests use different grading of particles, leading to added difficulties when comparing results. Barisone and Restivo (2000) verified that when very small sizes are used (e.g. in the 80°C AMBT), the structure of the rock may be destroyed during crushing leading to a false result.

Tests performed show that size and grading of aggregates have an influence on the reactivity. The influence on the formation of ASR products depends on the nature, texture and composition of the aggregate. There are different results, dependent on the aggregate being slowly reactive, rapidly reactive or showing pessimum content (Diamond and Thaulow, 1974).

For rapidly reactive aggregates, it was found that the amount of soluble silica was similar for different particle sizes of a certain aggregate, but the expansion varied for different size fractions, being larger for coarser particles (Multon et al., 2008). Also Zhang et al. (1999) concluded that for siliceous aggregates the smaller the particle size, the greater the ASR expansion when aggregate size is within the range 0.15-10 mm. They also state that the aggregate grading can affect the expansion of ASR: when there are larger aggregates in the specimen, the expansion is smaller at early ages, but will increase continuously at later ages. Also Hobbs and Gutteride (1979) concluded that for opaline rocks, expansion increases as the particle size decreases, when the reaction occurs at the surface of the particles. But when the reaction occurs within the particle, the rate of gel formation will be independent of the particle size. Lu et al. (2008) state that within a certain size range, the finer the aggregate particles of argillaceous dolomite limestone, the faster and higher the reaction rate and the expansion.

The aggregate reactivity is obviously dependent on the type of aggregate. The rate of reaction, the amount of products formed and the expansion are influenced by the aggregate type and also by the porosity (Ben Haha et al., 2007; Deng et al., 2008; Fernandes, 2009).

Mineralogy and texture are the main characteristics of an aggregate influencing the occurrence of ASR and the amount of gel produced (Lu et al., 2006a). Petrography should thus always be used as part of the documentation of aggregate reactivity.

There are several reports from field concrete confirming the occurrence of ASR and gel formation in concrete with slowly reactive aggregates (Shayan, 1993; Fernandes, 2009).

The composition of gel seems not to be dependent on the nature of aggregates. As stated by Thaulow et al. (1996), gel has high and varying contents of silica, lower and varying contents of calcium, low and relatively constant contents of alkalis and sometimes small amounts of aluminum, in agreement with other workers (Bérubé and Fournier, 1986; Brouxel, 1993). Gel with varied composition regarding the Ca content was identified in the same sample, with different composition from one grain to another and also in the same grain (Regourd and Hornain, 1986; Regourd-Moranville, 1989; Peterson et al., 2006; Fernandes, 2009). Calcium content is more prevalent in cracks found in the cement paste (Knudsen and Thaulow, 1975) than inside aggregates, developing a reverse trend to that of silicon. In cracks, Ca-rich gel is found at larger distance from the coarse aggregates, due to exchanges of alkalis with Ca in the cement paste. It has been verified that expansion does not necessarily increase proportionally to the reaction degree or the amount of gel produced, but it seems to be dependent on Ca content (Knudsen and Thaulow, 1975; Kawamura et al., 1998; Thomas, 1998).

By use of EDS, analyses of gel in field concrete with aggregates of variable composition/ mineralogy (granites and limestones) showed no significant difference in the gel composition (Fernandes, 2009).

There are just a few references in the literature discussing the influence of water absorption on the development of ASR products. Aggregates with higher porosity show a higher degree of reaction (e.g. sandstone, quartz with sub-granulation), because they are more easily penetrated by pore solution and have a higher specific area exposed to the solution (Bektas et al., 2004; Ben Haha et al., 2007). However, these pores and interstices could also store gel, influencing the expansion that could result from its formation.

Water absorption decreases the viscosity of the gel, but increases the amount of gel. The effect of water content on the gel viscosity is, among other properties, discussed by Bokern (2008) and ACI Committee 221 (2001).

Tests on specimens submerged in different salt solutions in the containers lead to the conclusion that the products formed differ in composition. NaOH is the more aggressive and produces a greater amount of gel, but KOH produces more crystalline gel (Lu et al., 2006b).

In the literature, it is reported that the expansion increases until a certain level of alkalis is reached and then decreases for higher alkali contents, concluding that there is a "pessimum" effect of external alkalis (probably related to available silica) (Kuroda et al., 2000).

To sum up; mineralogy and texture are the main characteristics of an aggregate influenceing the occurrence of ASR and the amount of gel produced. Petrography should thus always be used as part of the documentation of aggregate reactivity. In addition, particle size, grading and porosity of aggregates have an influence on their reactivity as well as on the rate of formation and the amount of ASR products. However, gel composition seems to be independent on the nature of aggregates.

6.3 Ettringite

For details, see Appendix 6.3.1 and 6.3.2

The occurrence of ettringite (and related reaction products like gypsum and thaumasite) in cracks and voids has frequently been reported from investigations of concrete exposed to - or tested in - moist environment. In the present context, it is however vital to distinguish between secondary formation (NB; definition not world wide acknowledged) and delayed formation of ettringite: Due to solubility, the former naturally follows from moisture movements and temperature changes, leading to (accumulating) deposits in air voids, cracks and porous areas like paste/aggregate interfacial zones and bleeding areas. Conditions inflicting frost or ASR damages clearly lead to secondary formation of ettringite. Its morphology differs from that of *delayed* ettringite formation, and its detrimental effects/forces (during reformation) have not been scientifically proven.

Delayed ettringite formation (DEF) on the other hand, is attributed to indirect effects of high temperature during early age curing: In stead of ettringite (AFt), the gypsum added in the cement mill to control the aluminate reaction reacts with the clinker aluminate phase (and water) to form monosulphate (AFm) due to inadequate SO_4^{2-} supply rate. The stability of these phases is temperature dependent, and later on and under ambient conditions, the AFm may react further, forming ettringite, i.e. delayed and imposing internal stress. The formation of DEF has not been demonstrated for concrete cured below 65°C, motivating temperature level regulations in concrete works execution standards accordingly. Hence, it is strongly recommended to consider this curing temperature limit for any performance test.

(Ettringite formation is also involved in the detrimental mechanisms caused by external sulphate attack, but requires a certain level of cement clinker aluminate content (C_3A) in addition to the external sulphate source.)

6.4 Influence of binder type on ASR products formed

The cement clinker type relatively affects the swelling ability of ASR gel due to the fact that the calcium ion content of the pore solution is related to the clinker type, especially the amount of alkalis present. ASR product in concrete tends to change in composition by time, accumulating calcium ions from the cement paste. The variation of calcium content is concerned with the age and location of ASR product in concrete (Diamond, 2000). However, the role of calcium ions on ASR expansion is uncertain. According to Powers and Steinour's theory (1955), ASR product has a swelling capacity if calcium over alkali ions ratio is low. Besides, for formation of a low expansive ASR product, some silica must diffuse through the reacted layers and water, as calcium ions and alkalis diffuse into the reaction zone. Wang and Gillott (1991) believe that the lime-alkali-silica gel is non-swelling, but argue that the presence of excess calcium hydroxide promotes the reaction. According to Chatterji (1986; 1989) and Chatterji and Thaulow (2000), calcium hydroxide accelerates the penetrations of sodium, calcium, hydroxyl ions and water molecules in a reactive grain. High Ca^{2+} ion concentration also lowers the diffusion of silicate ions out of the reactive grains. As a result, expansion occurs when more materials, i.e. Na^+, Ca^{2+}, OH^- and water enter a reacting grain than silica diffuse out. In a mixed electrolyte environment, e.g. calcium hydroxide and sodium chloride, more of the smaller ions, i.e. hydrated Na^+, follows the penetrating OH^- ions than larger hydrated Ca^{2+}, although both cations penetrate the reactive silica grains.

Prezzi et al. (1997) proposed a theoretical model based on Guoy-Chapman double layer theory, stating that the electrical double layer repulsive forces are responsible for the expansion of ASR products. The theory indicates that the larger the valence of the counter-ions in the double layer, or the larger the concentration of these ions, the smaller the double Prezzi et al. (1998) investigated the effect of chemical admixtures on ASR expansions by using AMBT test method. For a given initial molar concentration, the chloride salts with monovalent cations resulted in higher expansions, followed by the divalent and trivalent cations. Rodrigues et al. (2001) measured lower surface charge densities for opal in the presence of bivalent cations compared to the measurements in the presence of monovalent ions. Their results are in agreement with the double layer theory.

The consumption of $Ca(OH)_2$ by a supplementary cementing material reduces the damaging expansion regardless of the supply of reactive silica and alkali hydroxides. Thomas et al. (1991) investigated the composition of ASR gel in reactive flint aggregate containing concretes (one control sample and one incorporating fly ash) by using wavelength dispersive x-ray (microprobe) analysis. The control sample without fly ash exhibited cracking and deterioration, while the fly ash containing sample revealed no deterioration. For the control sample, the gel inside the reactive aggregate particles had Ca/Si ratios of 0.3, while the gel within the cracks in the paste had Ca/Si ratios higher than 0.9. Regarding the fly ash concrete, the Ca/Si ratio of the gel both within the aggregate and within the paste was 0.3, the gel dispersed into the paste without producing any damage to the concrete. It was concluded that the gel within the aggregate is initially low in calcium; this type of gel is fluid and can disperse within the paste without causing cracks. However, the availability of calcium ions within the paste (e.g. in the control sample) triggers its replacement with the alkali cations in the gel and increases the calcium content of the gel. Such a gel of higher Ca/Si ratio is more viscous and cannot dissipate easily within the paste upon absorbing water, leading to cracking. In the case of fly ash concrete, $Ca(OH)_2$ is reduced due to pozzolanic reaction and calcium is not available in the system, the low Ca/Si gel dissipates within the paste without giving any damage to the concrete. Similar conclusions were drawn by Arano and Kawamura (2000) after the BSE-EDS analysis of ASR gels in both control and fly ash incorporating mortars.

Bleszynski and Thomas (1998) investigated the gel formation of concretes cured in different alkali environments. In control samples without fly ash, high calcium silica gel is located at the periphery of reactive aggregate (flint sand). Amorphous high sodium silica gel is found in the interior of this high Ca layer followed by a crystalline high potassium silica gel. The high calcium silica gel is not observed in concrete incorporating 40% low-CaO fly ash, and the amorphous high sodium gel was found to have diffused into surrounding cement paste matrix without causing expansion or damage. The authors conjectured that the layer of high-Ca product that forms at the periphery of the flint grains in concrete without fly ash, does so because of the abundance of calcium hydroxide at the cement-aggregate interfacial transition zone and, that this layer acts as a semi-permeable membrane permitting the ingress of alkali ions and water into the aggregate, but preventing the exit of the alkali-silica gel resulting in osmotic pressures. The incorporation of 40% fly ash prevents the formation of this high-Ca layer thereby allowing the high-sodium gel to escape without building pressure. Expansion that occurs in fly ash containing concretes may be due to insufficient consumption of $Ca(OH)_2$ due to either ASR proceeding more quickly than pozzolanic reaction, low pozzolanicity of fly ash, high calcium content of fly ash and/or an insufficient quantity of fly ash.

Arano and Kawamura (2000) stated that at the early stages of ASR, the amount and composition of the gel produced does not seem to be affected by slag (ggbfs) addition; however, decreased expansions may be due to the decreased mobility of ions and reduced OH^- ion concentration of the pore solution. Zhao et al. (2008) suggests a different mechanism by analysing the pore chemistry of mortar samples. The authors suggest that the effect of slag is not reducing the alkali ion concentration of the system nor the mobility of ions, but produces a delaying effect by changing the gel composition for a temporary period.

In summary; The mechanism of ASR gel formation and its subsequent swelling is widely discussed in the literature. There are contradictory theories on the role of calcium ions. However, a change in the cement clinker composition, e.g. cement alkalinity and cement fineness, may lead to changes in the reaction products formed and their subsequent expansions. The beneficial effect of SCMs in decreasing expansions is widely discussed in this report. It should be noted that their mechanism of action is dependent on the type, amount, compound composition and fineness of the SCM.

6.5 Influence of mix design / casting on ASR products formed

It seems to be a good measure to decrease the water/binder ratio leading to a decrease in the permeability of concrete to prevent the ingress of water (that generates the swelling of ASR gel) or other destructive agents (e.g. external alkalis). However, there seems to be some disadvantages of this approach; lowering water content will also increase the pore solution alkalinity. The most suitable solution decreasing the porosity and the alkalinity of the system lies in the inclusion of a suitable supplementary cementing material and producing a high strength concrete with low permeability and low alkalinity (ACI Committee 221, 1998).

The studies carried out in field concretes support the superiority of high strength concrete. Katayama (2008) analysed the ASR gel of 6 deteriorated concrete structures in Newfoundland and laboratory concrete prisms by EPMA. His studies involved the effect of frost action as well as ASR in normal strength and high strength concretes. The amount of ASR gel in normal concretes were higher than in high strength prisms, and a narrow compositional range of ASR gel toward C-S-H gel in the [Ca/Si]-[Ca]/[Na+K] diagram. Furthermore, a trace amount of gel was observed in high strength concretes, even freeze-thaw action was superimposed.

Jensen et al. (1984) carried out an extensive research on the effect of air entrainment on ASR expansions by using 35 sand types of different reactivity degrees. The results show that the introduction of 4% air decreased the ASR expansions by about 40%. They observed the filling effect of air voids by ASR gel under SEM. There is no evidence of a gel composition change due to the incorporation of air voids. Hagelia (2004) observed a similar beneficial effect in the concrete cores from a retaining wall in Oslo, the effect seeming to be mechanical rather than chemical. There are some other findings in the literature that air entrainment is not beneficial in reducing ASR expansions (Fournier et al, 2009) – see also discussions in chapter 3.5 and 4.4. Further research on air-entraining concrete is needed, bearing in mind that the air-entrained concretes have lower strength that corresponding non-air-entrained ones and that the frost resistance of concrete also may decrease in the presence of ASR and frost action simultaneously.

Another important factor while interpreting the expansions of concretes affected by ASR, is the presence and dose of chemical admixtures. Most of the laboratory tests take the alkalinity levels of chemical admixtures into account. However, some chemical admixtures may also alter the expansion characteristics of ASR products. Among the superplasticisers tested, sulphonated naphthalene formaldehyde (SNF) and sulphonated melamine formaldehyde (SMF) seem to increase the mortar bar expansions (Wang and Gillot, 1989). However, the mechanism of this effect needs further research. Li et al. (2000) investigated the effect of calcium nitrate (CN) solution which is used to protect concrete from reinforcement corrosion and carbonation in the presence of fly ash and silica fume. CN solution addition improved the hydration process of concrete, less

$Ca(OH)_2$ is detected by XRD examination and higher chemically combined water is measured.

Kawamura and Fuwa (2003) stated that the average CaO/SiO_2 ratio of ASR gel is decreased and the gel composition became more homogenous by increasing the amount of lithium salts added. Sakaguchi et al. (1989) observed that the gel product in the presence of lithium is less soluble and more stable. This product hardly swells and forms a protective barrier around the aggregate preventing further attack. Some authors observed crystalline products of ASR, the EDS analysis revealing large amounts of Ca and Si ions, but less K ions (note that lighter elements such as lithium are not detectable by EDS techniques) (Mo et al., 2003; Collins et al., 2004). Tremblay et al. (2004) stated that the effectiveness of $LiNO_3$ in the presence of a reactive aggregate is due to the formation of a protective layer of well-crystallised lithium silicate at the aggregate surface.

Prezzi et al. (1998) explained the mechanism by using electrical double layer theory,.

Kurtis et al. (2000) examined the effect of LiCl on a sample of ASR gel from the FURNAS Dam, Brazil, in the presence of 0.7 M NaOH solution. In the presence of LiCl, the repolymerisation into an expansive gel was decreased when compared to the control sample.

There are still discussions in the literature about the mechanism of the suppressive effect of lithium salts. It seems that the lithium-silica reaction is more preferable when compared to alkali-silica reaction. This explanation also needs further research.

Alkali boosting may also affect the alkali content of ASR products depending on the type of the alkali.

To sum up; The effect of moisture on the expansion of ASR gel is obvious. Thus, it seems to be a good measure to decrease the water/binder ratio leading to a decrease in the permeability of concrete to prevent the ingress of water or other destructive agents, e.g. external alkalis into the concrete. However, there seems to be some disadvantages to this approach; lowering water content will also increase the pore solution alkalinity. The effect of air-entrainment is still not clear. These factors should be considered while evaluating the lab-field correlation of concrete mixtures.

7 Summary of influencing parameters

7.1 Internal humidity

During laboratory performance testing, the internal moisture content within the concrete prisms is aimed to be very high, i.e. higher than in most real concrete structures. Thus, the prisms should be subjected to “worst case humidity conditions” in the storage containers used. One main question is whether the test set up is able to secure a sufficiently high moisture level within the test specimens, regardless of binder composition and water/ binder ratio in the concretes tested. For binders with high self-desiccation, e.g. binders with low w/b ratio or binders with a high content of SCMs, this may be a challenge. As a result, the prism expansion may be reduced due to the lowered internal relative humidity (RH).

Other parameters that may increase the influence of self-desiccation, and thus contribute to maintain a rather low internal RH in the concrete prisms (even less than the critical RH needed for ASR to develop), are prism size (worse when increased), micro climate in the storage containers, length of pre-curing (reduced RH if prolonged due to a higher degree of hydration), permeability (less water uptake if low) and storage temperature (the degree of influence may vary dependent on the micro climate in the storage container). The aggregate porosity and the aggregate moisture state at the time of mixing may also be of importance, since use of rather porous and pre-wetted aggregates theoretically may totally counteract the effect of self-desiccation.

The test set up and the test procedures must also aim to avoid loss of water during storage and measuring. Important parameters in this respect are quality control (e.g. always use water tight lids), strict measuring procedures (measure quickly with as little moisture loss as possible), pre-cooling or not before measuring (the prisms will dry during cooling because moisture will move from the warmer inner part to the colder outer parts) and storage temperature (the higher storage temperature, the more drying during cooling). As a quality control, the mass of prisms should always be measured, evaluated and reported. If the mass increase during the test is too low, the test results should be questioned.

One important question has to be asked: *What is the most correct “reference length” to apply in ASR testing; the length after de-moulding, the shortest length after some shrinkage has occurred or the length after a pre-curing period?* The magnitude of the irreversible shrinkage will also influence this question.

7.2 Composition of the concrete pore solution

Available alkalis

The content of alkalis, i.e. sodium (Na^+) and potassium (K^+), in the concrete pore solution plays a major role for development of ASR. An increased alkali content leads to dissolution of more hydroxyl ions (OH^-) from $Ca(OH)_2$ and the pH of the pore solution increases. This higher alkalinity subsequently leads to dissolution of more reactive silica (SiO_2) from alkali reactive aggregates.

It has become standard practice to express the alkali content in terms of "sodium oxide equivalent" ($Na2O_{eq}$). There is, however, some discrepancy in the literature whether cements having a similar Na_2O-equivalent, but different K/Na ratios, perform differently regarding ASR. This may be of importance if reference CEM I cements are selected for laboratory performance testing.

As the degree of reaction is a function of the alkalinity of the pore solution, a high degree of alkali leaching during laboratory testing will lead to a poor laboratory/field correlation.

The reported *fixation of alkalis*, alkalis not available for alkali leaching, should be looked into further, along with the potential *enrichment and concentration of alkalis* in concrete structures. The issue of *recycling of alkalis* in the concrete should also be investigated further, as well as the main question of how to overcome the problem with *alkali leaching*. The feasibility of accelerated laboratory tests may depend on this.

Alkali leaching

Only a limited number of papers have quantitatively reported the extent of alkali leaching revealed with various concrete prism methods. Thus, more research is needed to contribute data in this area. Research studies have however revealed cases where up to 35% of the alkalis originally in the concrete found their way into water reservoir after 1 year (Thomas et al., 2006), while other studies present alkali leaching in the order of 2-10% of the original alkali content (Wigum, 2010; Lindgård, 2010). It is also revealed that alkali leaching is highest for specimens with the highest original alkali content.

It is clear that various storage conditions will influence the amount of alkali leaching, and potentially synergic effects between various conditions may occur. In particular the *prism size,* the *storage temperature* and any application of *wrapping* of the prisms may have a major influence on the extent of alkali leaching (Lindgård, 2010). Another issue of interest for further research is the extent of alkali leaching vs. the concrete *alkali content*.

Alkali release from aggregates

Some aggregate types may release significant amounts of alkalis to the concrete pore water and thus influence the ASR. Most of the 17 tested aggregate types from Canada contributed with alkalis in the range 0.45 to 0.70 kg Na_2O_{eq} per m^3 of concrete, but the amount varied from about 0.1 to 1.6 kg Na_2O_{eq} alkalis per m^3 of concrete dependent on aggregate type (Bérubé et al., 2000).

Ideker et al. (2010) showed that the contribution of alkalis from a “non-reactive” sand resulted in increased concentration of K^+ in the pore solution, elevated pore solution pH and a higher rate of expansion at early age compared to other “non-reactive” sands tested. The difference was most pronounced for the 60°C CPT. The choice of “non-reactive” sand in laboratory testing may thus influence the outcome of the tests.

The influence of w/b ratio, alkali boosting and pH on the extent of alkali release is also discussed in the report (chapter 3.5).

The task group “Releasable alkalis” in RILEM TC 219-ACS is presently trying to develop a reliable test procedure to measure the extent of alkali release from various aggregate types.

Binder type

The binder type is influencing the composition of the concrete pore solution that is mainly dependent on the alkalis available in the clinker. Low-CaO fly ashes reduce the pore solution alkalinity beyond mere dilution, whereas ground granulated blast furnace slag (ggbfs) can release alkalis to the pore solution. The extent is much less than that of clinker, and is almost independent of the alkali content of the ggbfs. Silica fume reacts fast and decreases the alkali concentration in the pore solution within the first two days of hydration, whereas the alkali concentration increases after 28 days up to 2 or 3 years, due to a reaction of calcium with the alkali-silica-gel and a release of alkalis to the pore solution.

The storage temperature and the length of the pre-curing period at 20°C may have a significant influence on the outcome of a performance test, in particular when SCMs are present. Both Fournier et al. (2004) and Schmidt et al. (2009) have documented that the concentration of sulphates in the pore solution is increased when elevating the storage temperature. Thus, the concentration of OH^- is reduced correspondingly. Primarily as a result of the drop in OH^- concentration, addition of only 10% fly ash to the binder was apparently able to suppress the expansion below the critical expansion limits for a highly reactive aggregate when exposed to 60ºC one day after casting (Schmidt et al., 2009). When pre-cured at 20ºC for at least 28 days before starting the 60ºC CPT, the concrete prisms with 10% fly ash expanded far beyond the critical limits.

The cement type or cement-SCM-combination influences the permeability of the concrete and thereby the rate of alkali leaching, the development of the OH^- concentration and the rate of expansion.

The rate of alkali leaching is much higher in small test specimens compared with massive concrete blocks or real structures in the field. This will influence the laboratory/field correlation.

Mix design/casting

The alkali content is one of the most important factors for ASR. Hence, all parameters that influence the alkali content have to be considered carefully, especially if the influence is likely to change the relationship between the laboratory and the field. Thus, well established, but non-performance test methods should not be adopted carelessly, for example by boosting the alkali level.

For a performance test, the same ”alkali-conditions” (i.e. identical type and amount of cement, chemical admixtures and any external alkalis; insignificant alkali leaching etc.) should preferably be used as will be used in the field.

Curing becomes more important for a performance test, especially when testing concretes with SCMs. With increasing curing time, temperature and RH, the hydration degree of the binder will increase, hence the paste will become denser, alkali leaching will be reduced, but the ingress of water and (possibly) de-icing solutions will also be reduced (Stark et al., 2008; Giebson, 2010b).

Increasing w/b ratio will result in a higher porosity (increasing the amount of capillary pores) and consequently internal transport processes will be accelerated, alkali leaching will increase and water or possibly other solutions will penetrate more easily (Kamali et al., 2003; Kamali et al., 2008). A decreasing w/b ratio will increase the OH^- concentration in the pore solution and vice versa (Stark et al., 2008). As discussed above, a reduced w/b ratio will also enhance the self-desiccation and reduce the internal RH in the concrete prisms. If the laboratory testing is performed with w/b ratios different from what will be applied in field, the laboratory/field correlation may be negatively influenced.

Air entrainment is important for concretes exposed to freeze-thaw cycles and de-icing solutions. In the literature, contradictory conclusions exist with respect to influence of the concrete air content on the ASR expansion. Jensen et al. (1984) and Hobbs (1988) showed that air entrainment addition was effective in decreasing the expansion due to ASR. The effect seems to be mechanical; air bubbles accommodate a portion of the ASR gel. Boyd et al. (2000) stated that the addition of a lightweight aggregate may show a similar behaviour. The same may be assumed to be the consequence if prisms for ASR testing are poorly compacted. However, other researchers have reported less or no influence of increased air content on the ASR expansion; Fournier et al. (2009) and FIB (unpublished results).

7.3 Properties of hydration products formed

Storage conditions
The storage conditions during laboratory testing influence the composition of the concrete pore solution, and will thus affect the laboratory/field correlation. High temperatures increase the rate of hydration and decrease the alkalinity of the pore solution, especially if applied to concrete compositions at young ages like in most ASR-tests. The impact is very distinctive if the concrete is made with cement with pozzolanic or latent hydraulic (ggbfs) materials or with combinations of cements and SCMs. As a consequence, the alkali-reactivity potential of a specific concrete mix may be underestimated. Therefore, some authors suggest applying a pre-storage at 20°C for at least 28 days before testing, to allow a normal hydration and a more realistic development of the concrete pore solution.

Aggregate type
The finest fractions of various aggregate types may be of significant relevance for the hydration products that form. This is due to the fact that very fine particles of certain rock types have the capability to react pozzolanically and hence increase the C-S-H phase. Examples of highly reactive materials being very effective pozzolans when crushed to fine particle size (finer than 63 microns) are Icelandic rhyolite and crushed bottle glass. These materials have a distinct amorphous silica phase.

An important finding by Pedersen (2004) was a significant temperature effect. Some rock fillers not being pozzolanic at ordinary curing temperature may be highly pozzolanic at a temperature of 80°C, e.g. fines from slowly reactive materials, such as Norwegian cataclasite and mylonite. The reason is that the silica phase in these slowly reactive materials is well crystalline. This fact is of high significance when using test regimes with high storage temperature. Testing of mortar or concrete mixes with significant amounts of fines from alkali reactive rocks may then give a "false negative" result if tested at very high temperatures. This is due to the fact that the pozzolanic reactivity increases with increasing temperature. Pedersen (2004) examined exposure temperature of 20, 38 and 80°C, and concluded that methods using 80°C should not be used for performance testing of real mixes. The effect of exposure temperature of 60°C such as the RILEM AAR-4.1 (RILEM, 2006) CPT was not investigated in that study.

Binder type
Some test methods that use elevated temperature might give misleading results for blended cement containing samples. High temperatures will activate the alkali binding capacity of SCM's and, especially at early stage, the pore structure and corresponding mass transport mechanism of the concrete is altered. It should also be noted that different types of SCMs might show different effects on the properties of the reaction products formed, mainly on Ca/Si ratio of C-S-H. More documentation is needed to correlate the field vs. laboratory performance of lithium incorporating concrete.

Mix design/casting
Irrespective of the type of curing, it was stated that changing the water/cement ratio will also change the Ca/Si ratio of C-S-H phases. Boosting the alkali level may alter the ettringite formed, and the reaction kinetics will change. It is also considered that all hydration products (and rate of their formation) are influenced by the humidity of curing and the curing period.

7.4 Aggregate reactivity

Storage conditions

Experiments show that the exposure temperature influences the aggregate reactivity. The solubility of SiO_2 increases with the temperature, a greater amount of gel is formed and higher expansion is observed at a given time since the reaction rate is accelerated by temperature. Nevertheless, normally lower ultimate expansion is obtained at higher temperature for similar specimens - see e.g. Fournier et al. (2004). This is assumed to be due to more alkali leaching (see chapter 3.2) and changes in the pore solution composition when elevating the storage temperature (see chapter 3.4). Thus, the temperature should not be analysed in isolation, as it works simultaneously with other factors.

High exposure temperature also seems to activate “non-reactive” aggregates (Shayan et al., 2008).

Fournier et al. (2008) performed field tests on concrete blocks in two different locations, one in Texas and one in Canada, to study the effect of temperature. They concluded that the expansion is faster and higher for the place with highest exposure temperature, but it depends on the type of aggregate selected. The difference in expansion increases with decreasing reactivity level.

The presence of alkalis has an influence on the reactivity of aggregates and on the extent of the reaction. Therefore, for a specific aggregate, more alkalis available mean more expansion, due to a higher concentration of OH^- in the concrete pore solution. For a specific test, it is verified that the result for the same aggregate may run from “innocuous” to “reactive” depending on the content of alkalis available for reaction.

It has been verified that different aggregates react in a different way when exposed to salt solutions, and also that the reaction is dependent of the type and concentration of the salt used (e.g. NaOH, NaCl, KOH or LiOH).

Aggregate type

Features associated with ASR are different for fine and coarse particles of a specific aggregate. Some aggregate types show higher expansion for larger particles, some for intermediate sized particles, and sometimes small particles produce more expansion.

Concerning the aggregates that exhibit pessimum behaviour, more reactive aggregates show maximum expansion for lower contents of reactive silica (Shayan, 1992; Bektas et al., 2004). The proportion applied during laboratory testing is thus of great importance.

The shape of the particles may also be of importance. Ramyar et al. (2005) found that the angularity of the particles has negligible effect on ASR expansion for very large and very small particles. However, for intermediate fractions, the angularity effect on ASR is more evident, and the effect of size of the particles is more pronounced in crushed aggregate.

The classification of non-reactivity is not universal. Tests performed with different “non-reactive” natural sands mixed with a specific reactive aggregate show different results depending on the test method applied and the laboratory conducting the test.

A main challenge today regarding identification of aggregate reactivity is to find an accelerated test that can correctly classify aggregates, in particular those considered non-reactive or slowly reactive. It is strongly recommended that all aggregates are classified by petrography before a performance test is executed.

Binder type
It is likely that a rapidly reacting aggregate, being further “accelerated” in a test, apparently will require another (stricter) degree of “measure” than a more slowly reacting one. To avoid development of ASR when testing a rapidly reactive aggregate type, the alkali content in the pore water must be lowered already in the early phase of the testing period. This is also compatible to the reported advantages of slag (ggbfs) and particularly fly ash with high reactivity (e.g. fineness) with respect to required dosage and aggregate reactivity (Thomas et al., 1995).

7.5 Reaction products formed during the exposure

Storage conditions
The most important storage conditions seem to be temperature and humidity, since these factors affect the pore solution chemistry as well as the rate of formation and expansion properties of ASR products, even though the morphology of the ASR-gel seems to be the same in laboratory specimens and in field concrete. Other important issues to consider are whether alkali boosting is applied or not in the testing procedure and the type of alkali compound used (contradictory findings for alkali boosting), since these two factors seem to alter the swelling properties of ASR products. Availability of restraint, size of test prisms and application of any wrapping seem to have secondary effects on gel properties.

ASR products
Mineralogy and texture are the main characteristics of an aggregate influencing the occurrence of ASR and the amount of gel produced. Petrography should thus always be used as part of the documentation of aggregate reactivity. In addition, particle size, grading and porosity of aggregates have an influence on their reactivity as well as on the rate of formation and the amount of ASR products. However, gel composition seems to be independent on the nature of aggregates.

Ettringite
The occurrence of ettringite (and related reaction products like gypsum and thaumasite) in cracks and voids has frequently been reported from investigations of concrete exposed to - or tested in - moist environment. In the present context, it is however vital to distinguish between secondary formation (NB; definition not world wide acknowledged) and delayed formation of ettringite: Due to solubility, the former naturally follows from moisture movements and temperature changes, leading to (accumulating) deposits in air voids, cracks and porous areas like paste/aggregate interfacial zones and bleeding areas. Conditions inflicting frost or ASR damages clearly lead to secondary formation of ettringite. Its morphology differs from that of *delayed* ettringite formation, and its detrimental effects/forces (during reformation) have not been scientifically proven.

Delayed ettringite formation (DEF) on the other hand, is attributed to indirect effects of high temperature during early age curing: In stead of ettringite (AFt), the gypsum added in the cement mill to control the aluminate reaction reacts with the clinker aluminate phase (and water) to form monosulphate (AFm) due to inadequate SO_4^{2-} supply rate. The stability of these phases is temperature dependent, and later on and under ambient conditions, the AFm may react further, forming ettringite, i.e. delayed and imposing internal stress. The formation of DEF has not been demonstrated for concrete cured below 65°C, motivating temperature level regulations in concrete works execution standards accordingly. Hence, it is strongly recommended to consider this curing temperature limit for any performance test.

(Ettringite formation is also involved in the detrimental mechanisms caused by external sulphate attack, but requires a certain level of cement clinker aluminate content (C_3A) in addition to the external sulphate source.)

Binder type

The mechanism of ASR gel formation and its consequent swelling is widely discussed in the literature. There are contradictory theories on the role of the calcium ions. However, a change in the cement clinker composition, e.g. cement alkalinity and cement fineness, may lead to changes in the reaction products formed and their subsequent expansions.

The beneficial effects of SCMs in decreasing expansions are widely discussed in this report. It should be noted that their mechanism of action is dependent on the type, amount, compound composition and fineness of the SCM.

Mix design/casting

The effect of moisture on the expansion of ASR gel is obvious. Thus, it seems to be a good measure to decrease the water/binder ratio leading to a decrease in the permeability of concrete to prevent the ingress of water or other destructive agents, e.g. external alkalis into the concrete. However, there seems to be some disadvantages of this approach; lowering water content will also increase the pore solution alkalinity. The effect of air-entrainment is still not clear. These factors should be considered while evaluating the laboratory-field correlation of concrete mixtures.

8 Conclusions

Assessment of influencing parameters

The comprehensive literature survey has been a joint work within the task group "Performance testing" in RILEM TC 219-ACS. Twelve authors have contributed to a various extent. In total, about 250 titles are included in the reference list. Our opinion is that all the main parameters of significant for ASR performance testing are included in the assessment.

The main focus in the literature survey has been to assess how various parameters may influence the laboratory/field correlation with respect to ASR performance testing, either directly on indirectly. More exactly the aim has been to evaluate how various *laboratory exposure conditions, aggregates types, binder types, mix designs* and *casting procedures* may influence the following important ASR related parameters;

- *Internal humidity* of the concrete prisms
- *Composition of the concrete pore solution* during testing
- *Properties of hydration products formed* during hydration / exposure
- *Aggregate reactivity*
- *Type and properties of reaction products formed* during exposure (i.e. primarily ASR-gel, but also any ettringite or delayed ettringite formation (DEF))

Parameters of high importance

The review revealed that the following ASR-related parameters are of high importance for the outcome of a laboratory performance test, and thus on the laboratory/field correlation:

- Internal relative humidity:
  - w/b ratio, self-desiccation, prism size, type of container, quality control
- pH of the concrete pore solution:
  - Alkali leaching, alkali release from aggregates, Na/K ratio, SCMs, pre-curing period, exposure temperature, alkali boosting
- Properties of hydration products:
  - w/b ratio, SCMs, pre-curing period, exposure temperature, pore structure, permeability, alkali binding capacity, fillers with pozzolanic effect
- Air-content:
  - Influence? lightweight aggregates, compaction
- Aggregate reactivity:
  - Exposure temperature, pH, humidity, salt solutions, grading, pessimum
- Reaction products:
  - Mineralogy and texture, exposure temperature, humidity, calcium

Need for further research

Based on the literature survey and on discussions in the task group "Performance testing" in RILEM TC 219-ACS, the following issues need further research:

- Parameters critical for drafting a performance test procedure set-up:
  - Internal moisture content; *does a critical lower w/b (=w/cm) ratio for performance testing exist? laboratory/field correlation for binders with high degree of self-desiccation?*
  - Alkali leaching; *extent dependent on test set-up and binder type? how to avoid alkali leaching? how to account for alkali leaching?*
  - Alkali boosting; *consequences dependent on mix design? accept a moderate boosting level?*
  - Elevated temperature; *total consequences for the outcome of a performance test? is 60°C reliable? aggregate – and binder dependency?*
  - Pre-curing period; *consequences? length required dependent on binder type?*

- General parameters, but not critical for the work in the “performance group”:
    - Self-desiccation; *what is the correct reference length for the test prisms?*
    - Pessimum aggregates; *test set-up?*
    - Slowly reactive aggregates; *test set-up?*
    - Alkali release from aggregates; *extent dependent of aggregate type and grading? test set-up (incl. grading)? consequences for the outcome of a performance test? laboratory/field correlation?*
    - Alkali content; *enrichment and concentration of alkalis? recycling of alkalis?*
    - Calcium; *role of calcium in ASR? laboratory/field correlation?*
    - Air content; *influence on ASR? how to test lightweight aggregates?*

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Distribution of work

	Parameter	Comment	2. Internal humidity			3. Composition of the concrete pore solution					
			Moisture content	Self desiccation (RH)	Shrinkage	Leaching	Alkali release	CaOH$_2$	$[OH^-]$	Alkali content	….
Storage conditions	Temperature	Curing	**Jan Lindgård and Bård Pedersen** **Appendix 2A - 2B - 2C** **(Chapter 2)**			**Børge J. Wigum and Jan Lindgård** **No appendix** **(Chapter 3.1 and 3.2)**					
		Exposure									
		Measuring									
	Humidity	Above water									
		Submerged									
		With alkalis									
	Wrapping	Water amount added									
	Prism size										
	Type of container	Stable water level?									
	Time										
	External alkalis										
Aggregate type	Slowly reactive	Grading/size distribution				**Maarten Broekmans** **No appendix** **(Chapter 3.3)**					
		Mineralogy									
	Fast reactive	Grading/size distribution									
		Mineralogy									
	Pessimum?	Grading/size distribution									
		Mineralogy									
	NR-reference	Non-reactive??									
	Water absorption										
	ACR	Not included in ACS-P									
	Filler type										
Binder type	Type of clinker	Mineralogy, Blaine				**Ingmar Borchers, Isabel Fernandes and Özge Andiç-Çakır** **No appendix** **(Chapter 3.4)**					
	Silica fume										
	Fly ash (PFA)										
	Slag (ggbfs)										
	Other SCMs?	incl meta kaolin									
	Other										
	…..										
	…..										
Mix design/casting	Water/binder ratio	Diffusion properties				**Colin Gibson** **Appendix 3.5** **(Chapter 3.5)**					
		Porosity									
	Air content	Porosity									
	Aggregate moisture content										
	Binder content	Volume cementitious paste									
	Alkali boosting	NaOH									
	Curing (before exposure)	Temp./moisture/time									
	Type of end studs										
	Form oil										
	Chemical admixtures	incl. lithium									
	Workability										

Distribution of work

	Parameter	Comment	4. Properties of hydration products formed (incl pozzolanicity, ….)							5. Aggregate reactivity	6. Reaction product formed during the exposure		
			CEM I	Silica fume	PFA	Slag	Meta kaolin	Other SCMs	Fillers…		ASR-gel	DEF	Ettringite
Storage conditions	Temperature	Curing	**Ingmar Borchers** **Appendix 4.1** **(Chapter 4.1)**							**Isabel Fernandes** **Appendix 5** **(Chapter 5.1 and 5.2)**	**Eric Brouard: Appendix 6.1A** **Isabel Fernandes: Appendix 6.1B** **(and Özge Andiç-Çakır)** **(Chapter 6.1)**		
		Exposure											
		Measuring											
	Humidity	Above water											
		Submerged											
		With alkalis											
	Wrapping	Water amount added											
	Prism size												
	Type of container	Stable water level?											
	Time												
	External alkalis												
Aggregate type	Slowly reactive	Grading/size distribution	**Bård Pedersen** **No appendix** **(Chapter 4.2)**								**Isabel Fernandes** **Appendix 6.2** **(Ch. 6.2)**	**Appendix 6.3.1** **(Ch. 6.3)**	**Appendix 6.3.2** **(Ch. 6.3)**
		Mineralogy											
	Fast reactive	Grading/size distribution											
		Mineralogy											
	Pessimum?	Grading/size distribution											
		Mineralogy											
	NR-reference	Non-reactive??											
	Water absorption												
	ACR	Not included in ACS-P											
	Filler type												
Binder type	Type of clinker	Mineralogy, Blaine	**Özge Andiç-Çakır** **No appendix** **(Chapter 4.3)**							**Terje F. Rønning** **No appendix** **(Chapter 5.3)**	**Özge Andiç-Çakır** **No appendix** **(Chapter 6.4 and 6.5)**		
	Silica fume												
	Fly ash (PFA)												
	Slag (ggbfs)												
	Other SCMs?	incl meta kaolin											
	Other												
	…..												
	…..												
Mix design/casting	Water/binder ratio	Diffusion properties	**Christian Pierre (and Özge Andiç-Çakır)** **Appendix 4.4** **(Chapter 4.4)**							**Assumed covered elsewhere in the report**			
		Porosity											
	Air content	Porosity											
	Aggregate moisture content												
	Binder content	Volume cementitious paste											
	Alkali boosting	NaOH											
	Curing (before exposure)	Temp./moisture/time											
	Type of end studs												
	Form oil												
	Chemical admixtures	incl. lithium											
	Workability												

The questions, hypothesis and statements are given under the supposition that the laboratory testing must secure a high internal humidity within the concrete. This means that the internal moisture content is aimed to be higher than in most real concrete structures, i.e. the tested concrete recipes and binder types are given "worst case humidity conditions" in the laboratory testing.

Moisture content			
Line No.		**Question / hypothesis / discussion**	**Ref. No.**
Storage conditions	1-2	- The susceptibility for loss of moisture in accelerated ASR laboratory testing will increase with increasing temperature. The possible weight loss is controlled by the relative humidity (RH) in the surroundings. If concrete prisms are placed in containers stored in a dry environment, e.g. as in the RILEM AAR-3 concrete prism test (CPT) [1], the risk of drying increases (see A10). - The curing temperature may influence the concrete porosity and permeability. A higher curing temperature will normally lead to a coarser porosity and consequently an increased permeability, as reported by Kjellsen et al. [2]. As a consequence, the applied curing and storage temperature may influence water uptake, water transport and drying properties, and thus also the internal moisture content during accelerated laboratory testing. - For a given concrete, the sorption properties and the internal RH are to a certain degree dependant on the temperature. A raised temperature in a part of a concrete sample/structure will lead to an increase in the local vapour pressure. This will initiate moisture transport and, eventually, reduce the local moisture content, and as a consequence lead to a decrease in RH, as discussed by Nilsson [3]. However, if the moisture content within a concrete is constant, a general increase in the temperature will give rise to a small increase in the internal RH. Example; According to tests reported by Sjöberg et al. [4] the RH within a concrete with w/c 0.40 and internal RH 90 % will increase approx. 0.25 % per °C. Thus, an increase of the concrete temperature from 20°C to 40°C may increase the internal RH with approx. 5 %. The effect decreases with increasing internal RH and with increasing w/c-ratio [3,4]. One consequence of this phenomenon is that the internal RH in concrete prisms will increase with increasing storage temperature provided no change in the concrete internal moisture content.	[1-4]
	3	- The prisms may loose significant quantities of water during cooling to room temperature before measuring, and also during measuring of length and weight. The main mechanism for the outwards transport of water is the higher local vapour pressure in the interior of the prisms due to a higher temperature (see A1-2). Parameters influencing the extent of drying are storage temperature (worse if high), prism size (worse if thin – see A8), measuring time (worse if long) and possible application of wrapping (worse if unwrapped). Preliminary tests performed by Lindgård [5] showed that the water loss during cooling of $70\cdot70\cdot280$ mm^3 unwrapped concrete prisms from 60°C to 20°C in RILEM AAR-4 containers [6] corresponded to a reduction in the degree of capillary saturation (DCS) of approx. 4.5 % (cement type CEM I; w/c-ratio 0.48). For prisms stored at 38°C the corresponding loss of water was only 1/4 (unwrapped) and 1/8 (wrapped), respectively, compared to the unwrapped prisms stored at 60°C.	[5-6]

Moisture content			
Line No.		**Question / hypothesis / discussion**	**Ref. No.**
Storage conditions	4	- The micro climate in the storage container is of great importance. It is essential to obtain a homogenous and high RH in the containers. Important parameters are size and design of storage containers, type of lining and application of a watertight sealing. Example; The Norwegian 38°C CPT (prism size 100·100·450 mm^3) was not included in the Norwegian optional arrangement for acceptance and approval of aggregates in the period 1993-2004. The reason was that certain sedimentary aggregates tested in the early 90'ties exhibited non reliable results, i.e. was not in accordance with field experience (deleterious expansion if field, but not in the laboratory). Later studies revealed that the most likely reason for the discrepancy was the use of large storing containers where humidity could not be controlled satisfactory [7,8] (see A9).	[7-8]
	5	- Submerging will give rise to a high internal water content during storage, unless large test specimens and a low w/c-ratio are applied (see A29-30). One consequence of the likely higher moisture content in submerged concrete prisms, compared to most field concrete structures, is development of a less swelling gel due to a reduced viscosity. The effect of water content on the gel viscosity is among others discussed by Bokern [9] and ACI Committee 221 [10]. - Another important consequence of submerging, also leading to reduced expansion, is enhanced leaching of alkalis (see Appendix 3) provided submerged in water.	[9-10]
	6	- High alkali contents within the concrete pore water may reduce RH [11], but in this setting we believe that the influence of external added alkalis on the concrete RH is neglect able compared to the influence of other parameters.	[11]
	7	- Wrapping of concrete prisms, by use of moist cotton cloths and plastic sheets, may reduce access to ambient moisture in the air. If the wrapping effectively hinders contact between the ambient moisture content in the storage container and the prisms (e.g. as in the RILEM AAR-3 CPT, where the wrapped prisms are stored in plastic bags [1]), the amount of water added during the wrapping procedure and on top of the prisms at every measuring time may have high influence on the internal moisture content within the concrete prisms. Example; In a round robin testing program being part of the Canadian testing of the Spratt aggregate, significant difference in expansion and weight increase of concrete prisms was revealed between two Norwegian and one Icelandic laboratory using the RILEM AAR-3 CPT. The main differences in the testing arrangement were the type of wrapping material applied and the amount of water added to the wrapping before sealing the plastic bags [5]. - Wrapping will reduce evaporation during cooling and measuring (see A3).	[1,5]
	8	- If the size of concrete specimens increases, the probability for development of a moisture profile through the cross-section will increase. In particular this is the case for large concrete field cubes and massive concrete structures. Several authors, e.g. Stark [12] and Sellevold [13], have shown that moisture fluctuations in field basically take place in the outer layer (some cm's) of the concrete. The depth of the influenced zone will decrease with decreasing w/c, see e.g. Yang et al. [14], due to a reduced permeability. As a consequence, the residual concrete mix water, depending on the w/b-ratio (see A29-30), rather than ambient wetting and drying determines the prevailing moisture content in the interior of massive concrete structures, as discussed by Stark [15]. For such structures the extent of self-desiccation, mainly controlled by the w/c-ratio, may govern the interior RH level of the concrete (see B8). - The risk of losing moisture from concrete prisms during testing is assumed to decrease with increasing prism cross-section due to a reduced surface/volume-ratio.	[5, 12-15]

Moisture content			
Line No.		**Question / hypothesis / discussion**	**Ref. No.**
		However, in a test performed by Lindgård, $100 \cdot 100 \cdot 450 mm^3$ prisms (surface/volume-ratio 0.44) lost similar quantity of water as $70 \cdot 70 \cdot 280 mm^3$ prisms (surface/volume-ratio 0.64) during cooling from 38 to 20°C before measuring (v/c=0.45; see A3) [5].	
Storage conditions	9	- Type of storage container will influence the distribution of moisture and thus the RH in the air inside the container. Large containers may for instance lead to a poor distribution of moisture. The experience gained with the Norwegian 38°C CPT when large storage containers holding several concrete prisms were replaced by smaller containers holding only 3 prisms in each, was a general increase in expansion. With the introduction of the smaller containers also the Norwegian sandstone, proven to be reactive in field, showed expansions above the critical limit [8]. (See also A4).	[8]
	10	- The storage time influences the sensitivity to loss of water, in particular if the containers are stored in a dry environment (see A1-2). For instance have SINTEF experienced that RILEM AAR-3 containers [1] are particular vulnerable to drying due to the small amount of water in the bottom of the containers (only 350 ml) combined with a long testing time (one year).	[1]
Aggregate type	19	- The aggregate water absorption may influence the internal moisture content in the concrete, in particular for concretes with a low w/c ratio. A highly porous aggregate may supply the paste with a considerable amount of moisture during the curing and exposure period, and thus counteract the internal drying due to self-desiccation. E.g. can addition of wet light weight aggregate particles be applied as a tool to reduce the autogenous shrinkage caused by self-desiccation, as shown by Lura et al. [16] and Hammer et al. [17]. Theoretically only 15 l/m^3 of extra water is needed to fill the empty pore space generated by cement hydration (self-desiccation pores) of a concrete with w/c 0.40, 400 kg/m^3 cement and 65 % degree of hydration [17]. As a consequence, also the extent of water absorption of normal weight aggregates may influence the internal RH in a concrete. As Hammer et al. conclude [17], a saturated aggregate with 0.8 % water absorption may theoretically supply a "w/c 0.40 concrete" with sufficient moisture to totally counteract the drying due to self-desiccation (see also A32 and B32). However, also the aggregate pore structure relative to that of the cement paste is of importance. As Hammer et al. discuss [17], the two faces combat for water. The winning phase is the one with the smallest pore structure, since smaller pore structure produces smaller capillary meniscus and thus greater tension in the water. The volume decrease associated with chemical shrinkage of the cement paste will also create pore water tension that helps the cement paste.	[16-17]
Binder type	21-27	- Type of binder may influence the permeability of the concrete, and thus also the water uptake and the sensitivity to drying during exposure and measuring (see A1-3). The extent of self-desiccation, and as a consequence the internal RH, may also vary depending on type of binder (see B22-26). - By use of supplementary cementing materials (SCM's) the effect of increased temperature (see A1-3) on the properties of the concrete is believed to be higher. In particular the temperature may influence the properties of hydration products formed during hydration (see Appendix 4) and the rate and extent of hydration. As a consequence, the effect of curing - and storage temperature on internal transport properties, and thus also on the internal humidity, may to some extent be dependent on the type of binder applied. (See also A35).	

Mix design/casting	29-30	– The sensitivity to drying during exposure and measuring (see A1-3) will decrease with decreasing w/c, due to a reduced and refined porosity and as a consequence a reduced permeability. However, also the ability to suck water will be reduced with decreasing w/c, as shown by Kvalvik et al. [18]. In these tests, drying properties of concrete floors were investigated. The parameters varied were concrete composition (w/c-ratio, cement type and binder content) and curing conditions (varying between the extreme points water on top for seven days before start drying to no covering of the concrete surface after casting). The measurements showed that the internal RH in the concretes with w/c 0.40 was almost independent of the curing conditions, in contrast to the concretes with w/c-ratio 0.60. The concretes with w/c-ratio 0.50 responded somewhere between these high – and low quality concretes to the addition of moisture on the top surface. - At low w/c it may be difficult to secure a sufficient high moisture content within the concrete due to a high degree of self-desiccation (see B29-30), in particular for rather massive concretes (e.g. outdoor stored cubes) and maybe also for rather large laboratory test specimens. For such structures/specimens the extent of self-desiccation may govern the interior RH level of the concrete [14-17,19,20,21,22] (see also A8 and B8), and thus influence the extent of damage due to ASR. An example: In tests performed by Sellevold & Justnes [20] the internal RH in sealed cement paste samples with water/binder-ratio varying from 0.20-0.40 was in the range 80-90 % after approx. two weeks of hydration. The critical limit for developing ASR is reported to lie in the same range depending on several factors, as discussed by Larive [23].	[14-23]
	32	- The amount of water within an aggregate may have a considerable influence on the RH within the concrete, in particular for concretes with a low w/c ratio (see A19). - If a dry, porous aggregate is applied in the concrete mix, water may be sucked from the paste into the aggregate during and after the time of mixing. This may lead to casting problems (more water and/or superplasticizer is required) and a somewhat reduced water content in the cement paste. Later in the curing period the aggregate particles my supply the paste with water, thus counteracting the effect of self desiccation [16,17] (see also B32).	[16-17]
	35	- The curing conditions of the concrete are of importance for the internal concrete moisture content. As reported by Kjellsen et al. [2], an elevated curing temperature (e.g. by exposing the prism to 60°C directly after demoulding) will normally lead to a coarser porosity and consequently an increased permeability in the long run (see A1-2). This may obviously influence the internal humidity and transport properties. - If pozzolanic materials are applied as a tool to combat ASR, an early elevated temperature may particularly influence the outcome of an accelerated performance test. An important question, discussed by Bokern [9], is whether elevated temperature accelerates the pozzolanic reaction more than the ASR. If so, the outcome of the laboratory test may be too positive compared to expected long time field behaviour (see also Appendix 4). As a consequence, Bokern recommends allowing the concrete to hydrate sufficiently, e.g. 28 days at 20°C, before starting the AAR testing. A prolonged curing time may, however, also influence the concrete internal humidity. If rather large concrete prisms (e.g. cross-section 100·100 mm^2) and a low w/c ratio are applied, the combination of high degree of self-desiccation and a dense, well cured concrete may lead to a permanent rather low internal RH in the prisms (see A29-30).	[9]
	37	- If a "wrong type" of form oil and/or too much form oil is applied during casting of concrete prisms, the sorption properties of the concrete surface may be influenced, thus reducing the ability to absorb water from the ambient air.	

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The questions, hypothesis and comments are given under the supposition that the laboratory testing must secure a high internal humidity within the concrete. Thus, the moisture content will be higher than in most real concrete structures, i.e. the recipes and binder types are given "worst case humidity" in the laboratory testing.

Self desiccation			
Line No.		**Question / hypothesis / discussion**	**Ref. No.**
Mechanisms		**Mechanisms causing self desiccation:** The hydration process of the cement gives a reduction of the volume. This is due to the fact that the reaction products (C-S-H gel) have a smaller volume than the reactants (cement + water). This phenomenon is referred to as *chemical shrinkage*, and has some major effects: 1) It causes *autogenous shrinkage*, which is a volume contraction of the total concrete body. In the plastic phase, the chemical shrinkage equals the autogenous shrinkage. 2) In the hardening phase, the chemical shrinkage causes empty pores within the concrete. These pores will be left empty if no water is supplied from the surroundings. This leads to a lowering of the RH in the concrete, a phenomenon called *self-desiccation*. At low w/c ratios (<0.40) this effect is large (may e.g. be able to reduce the RH below 80 % during a couple of weeks). 3) When water is gradually consumed during the hydration process and the chemical shrinkage pores are left empty, the remaining water will be in a state of "tension stress". This is the mechanism explaining the autogenous shrinkage in the hardening state. In this section, the effects of self desiccation on the RH or moisture content will be treated. The direct effects of autogenous shrinkage will be treated in Appendix 2C (together with the effects of drying shrinkage).	[10-12]
Storage conditions	1-2	- Elevated temperature in the early hardening phase will increase the hydration rate, which will lead to self desiccation at an earlier point of time. This may lower the resulting RH if the self desiccation pores are not allowed to be filled during the curing/exposure period. A consequence could be a reduction, or at least a time delay, in the resulting expansions due to AAR.	
	5	- Submerging will counteract, and in most cases likely totally hinder, a reduction of the RH due to self desiccation. However, Nilsson [5] has shown that submerged high performance concrete (w/c approx. 0.30) may not be saturated due to self desiccation and extremely slow moisture transport into the concrete. (For practical purposes, a combination of thick specimens and low w/c may hinder pore filling of water).	[5]
	7	- If a water tight wrapping is applied, the RH within the concrete may be more controlled by self desiccation (because the prisms are less able to take up water from the ambient moisture content within the storage container). The initial curing (time and conditions) then becomes more important to secure a high RH. - The effect increases with decreasing w/c. For practical purposes the effects of self desiccation becomes important for concretes with w/c ≤ 0.5.	[10]

Storage condition	8	- Increasing prism size will increase the influence of self desiccation on the concrete RH. If for instance large concrete cubes are cast for outdoor storage, the influence of self desiccation on the RH is assumed to be high. - In general, at depths > 50 mm from the surface layer of the concrete, the RH is basically controlled by the self desiccation and to a very low degree by the surroundings of the concrete body.	[1]
	11	- See A6.	
Aggregate type	19	- The aggregate water absorption may influence the internal concrete RH, and thus the degree of self desiccation – see A19, A32 and B32.	
Binder type	21	- Different Portland cements may lead to different self desiccation. An important parameter is the fineness (Blaine) of the cement. - Finer cements and higher amounts of C_3A and C_4AF may lead to increased self desiccation and autogenous shrinkage.	[5,6,8] [10]
	22-26	- Use of pozzolans and slag may increase the self desiccation and thus reduce the internal RH, in particular if the prisms are wrapped and / or partly sealed. - Silica fume and fly ash may increase the self desiccation.	[7] [11]
Mix design/ casting	29-30	- The self desiccation will increase with decreasing water/binder ratio (see example in A29-30). Thus, the concrete RH may for some test arrangements be controlled by the w/b-ratio of the concrete, in particular if a large prism size and a water tight wrapping is applied. - *Should there for performance testing of job mixes be set a lower limit for the water/binder ratio? i.e. not allowed to perform tests below this* w/b_{limit} *(= 0,40??).* - According to Lagerblad & Trägårdh [9], there could be differences for quickly and slowly reactive aggregates with respect to the effect of w/c (tested by the Danish NT build 295….). *Does slowly reactive aggregates need more water to react?* - It is known from earlier that Norwegian sandstone is particularly sensitive to the moisture condition [3] (see also line 9 in Appendix 2A). - *(Experience of field performance versus lab.-performance of low w/c concrete will hopefully be summarized by B. Fournier during 2009 as part of his survey of the outdoor stored concrete cubes at CANMET in Ottawa).*	[6,7] [9] [3]
	32	- High aggregate water content may counteract a reduction in the RH caused by self desiccation – see A19, A32 and B19. The self desiccation may be eliminated, even for a low w/c concrete, if highly porous and wetted aggregates are used [4].	[4]
	35	- The curing time and the moisture conditions during curing (submerged or sealed or something between?) are of importance for the effect of self desiccation and thus for the concrete RH. - Submerged curing during the first weeks may counteract at last some of the effect of self desiccation. The importance of curing increases with decreasing w/b. - For very low w/c concretes, submerged curing may not be sufficient to give high enough RH (see also B5).	[5]

	38	- *May some admixture types influence the self desiccation of the concrete significantly? (and thus influence the concrete RH?).* No relevant literature was found on this topic. - *Will lithium influence the self desiccation of the concrete?* In the paper by Millard and Kurtis [13] this question is, among other factors, looked into. Some results indicate that lithium nitrate dosages accelerate early chemical shrinkage and hydration. Generally, as the lithium dosage increased, less autogenous shrinkage was observed in the first 10 days. Often, a net expansion occurred in the first 24 h. After 28 days, pastes with the highest (400%) dosages exhibited significantly greater autogenous shrinkage than the control samples. However, in all conditions examined, pastes produced with the standard dosage of lithium nitrate (100% dosage) did not exhibit significantly more autogenous shrinkage than the corresponding control (no lithium) mixes. However, it is worth noting that one of the low alkali cements, where early hydration was most accelerated by lithium nitrate addition, shows the least effect of lithium addition on autogenous shrinkage. Thus, further research is necessary to completely understand the relationships between hydration, microstructure development and autogenous shrinkage with the addition of lithium nitrate. Overall, the results suggest that lithium nitrate admixtures are likely innocuous when used at recommended dosages rates, for most cements. However, additional testing may be warranted to examine early setting, heat evolution, and shrinkage, for critical applications, particularly with low alkali cements. In general, however, variations in behaviour were greater between the six different cements than with increasing lithium nitrate admixture dosage for a particular cement.	[13]

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Internal humidity - Shrinkage

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The questions, hypothesis and comments are given under the supposition that the laboratory testing must secure a high internal humidity within the concrete. Thus, the moisture content will be higher than in most real concrete structures, i.e. the recipes and binder types are given "worst case humidity" in the laboratory testing.

Shrinkage			
Line number		**Question / hypothesis / discussion**	**Ref. No.**
Mechanisms		**Mechanisms of volume changes:** A number of different mechanisms may lead to volume changes of concrete, both in the plastic phase and in the hardening phase. Relevant mechanisms for the hardening phase which will be treated further are: - Autogenous shrinkage (see also Appendix 2B) - Drying shrinkage - Temperature movements The magnitude of shrinkage may be relatively high compared to the measured length increase caused by AAR. A couple of examples: - Self desiccation shrinkage of a concrete with w/b 0.35 may be in the order of 0.01 % after one week curing [1]. - Long-term drying shrinkage in dry conditions (RH of 50 %) may be higher than 0.1 % [2,3] - Long term drying shrinkage may be in the order of 0.04 % when stored in 80 % RH [3].	[1-3]
Storage conditions	1-2	- Increased curing temperature will accelerate the hydration rate and may lead to increased shrinkage during the first days and weeks of curing. This is relevant for the reference measurement of length.	
	3	- Whether the prisms are cooled or not prior to measurement may be of significance. If the prisms are cooled before they are measured, this may lead to loss of moisture leading to shrinkage. This effect will be less for wrapped prisms due to lower weight loss during cooling (see A3).	
	5	- No drying shrinkage if submerged, rather a tendency towards swelling. - Generally, the total shrinkage can be divided into one reversible part and one irreversible part.	[3]
	3-4 7-10	- The extent of shrinkage is dependent on the loss of moisture (drying shrinkage) and the reduction in the internal RH due to self desiccation. ***- One major question:*** *What is the most correct "reference length", the shortest length after some shrinkage has occurred or the length after de-moulding?*	
Aggregate type	19	- Porous aggregates with high water absorption may act as a water supply and counteract shrinkage (se also A19). - The aggregate generally act as a restraint, and generally increased aggregate content reduces the shrinkage. - The type of aggregate itself may have some significance for the magnitude of shrinkage, because aggregate affects the E-modulus of concrete. Higher E-modulus generally gives lower resulting shrinkage. - Some aggregates may shrink themselves, and some types of dolerite, greywacke, basalt and mudstone may give a much higher potential of shrinkage than concrete with granite, limestone and quartz aggregate.	[3]

Binder type	21-27	- The extent of shrinkage is dependent on the loss of moisture (drying shrinkage) and the reduction in the internal RH due to self desiccation. Thus, the binder type is of importance for the magnitude of the total shrinkage that may occur, due to the influence on the concrete permeability and degree of self desiccation (see A21-27 and B21-27).	
Mix design/ casting	29 30 32 35	- The autogenous shrinkage will increase with decreasing w/c-ratio due to higher self-desiccation (see B29-30). - The possible drying shrinkage generally is lower for lower w/b ratios (see also A29-30).	[3]
	33	- The extent of shrinkage will increase with increasing binder content (if loss of moisture or reduced RH).	[2]
	38	- Some admixtures may increase the extent of shrinkage	[3]

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Influence of mix/design casting on the composition of the concrete pore solution

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	Alkali leaching	
Line number	**Question / hypothesis / statements**	**Reference numbers**
29, 30	- the w/b-ratio clearly influences the leaching behaviour - increasing w/b-ratios will result in a higher porosity (more capillary pores) which means faster and more leaching - low w/b-ratio should result in reduced leaching - the w/b-ratio for the performance-test should clearly be set as used for the field concrete	[1, 2]
31	*Do artificial air voids, introduced by air entraining agents, influence leaching?* - air entrainment is important for concretes exposed to freeze-thaw cycles and should clearly be considered in the performance-test - it was found that artificial air voids (space for the gel) are able to reduce expansion to some extent (often found in laboratory investigations), but it was also reported that artificial air voids in some cases (outdoor exposure) have no significant effect or even result in higher expansion - so far, air-entrainment does not have a clear effect on expansion - there are virtually no investigations available about the influence of air-entrainment on leaching	[3, 4]
32	- dry aggregates with a high porosity (e.g. as known for some gravels) will absorb some of the mixing water, what could reduce the w/b-ratio (porosity) and consequently leaching - high-porosity aggregates with a high moisture content could provide additional water and consequently support leaching due to greater dissolution of alkalis - BUT: the water absorption capability of aggregates is usually well considered in the field as well in the laboratory, hence the parameter seems to be insignificant	
33	- with increasing binder content a greater depot of alkalis is available, hence a sufficient amount of alkalis could remain in the concrete despite of leaching during the test - a high binder content results in a greater portion of cement paste in the concrete, and because virtually all transport processes in the concrete take place in the cement paste and the paste/aggregate boundaries, the kinetics of leaching will be influenced - for a performance-test, a higher binder content (compared to the job mixture) should not be used to compensate leaching	

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Author: Colin Giebson, Finger-Institute, FIB

34	- alkali boosting will provide a greater depot of alkalis, hence a sufficient amount of alkalis is available despite of leaching - alkali boosting will probably not influence the kinetics of leaching - the effect of alkali boosting on expansion also seems to depend on the type of aggregate - it seems like some aggregates are more sensitive to alkali boosting than others, what supposes that different mechanisms are running - depending on the type of alkalis added, boosting could initiate different mechanisms that probably will not appear in the field - boosting should not be an option for a performance-test - but the upper limits (variations) of alkali and cement content that can be expected in the field should be considered	[4]
35	- with increasing curing time, temperature and RH, the hydration degree of the binder will increase, hence the paste will become denser and leaching could be reduced (significantly?) during the test, especially for SCM-containing concretes	
36	- insignificant	
37	- oil that remains on the prism surface may reduce leaching, but also water absorption	
38	- a possible influence depends on the type of the chemical admixture added - e.g. superplasticizers will give a more dense concrete structure - also see line 31: air entraining agents could have some influence - finally: in a performance-test, the same chemical admixtures as used in the field should preferably be used.	
39	- bad workability that result in an less dense concrete structure may support leaching	

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Influence of mix/design casting on the composition of the concrete pore solution

Author: Colin Giebson, Finger-Institute, FIB

Release of alkalis from aggregates		
Line number	**Question / hypothesis /statements**	**Reference numbers**
29, 30	- the amount of the alkalis released depends strongly on the type of aggregate - with decreasing w/b-ratio the pH increases and the cement paste is getting denser - (1) with increasing pH (especially > 13) the release of alkalis from aggregates increases due to the stronger attack (increased solubility of alkali-minerals) - (2) the major factor that influences the maximum alkali release is the pore solution/aggregate ratio: in a dense cement paste (low w/b), water transport and ingress is reduced and consequently the release of alkalis from aggregates is reduced too (i.e. in contrast to (1))	[5]
31	- insignificant	
32	- dry aggregates with a high porosity (e.g. as known for some gravels) will absorb some of the mixing water (pore solution), what could promote an “internal” dissolution of alkali-minerals and increase the total release of alkalis (Is this significant?) - high-porosity aggregates with a high moisture content could provide additional water what consequently could support the dissolution of alkalis - BUT: the water absorption capability of aggregates is usually well considered in the field as well in the laboratory, hence the parameter seems to be insignificant	
33	- increased cement content (not SCMs) also means higher content of alkalis/OH^-, so the attack of the aggregates (alkali-minerals) is supported - a high binder content results in a greater portion of the cement paste in the concrete and because virtually all transport processes in the concrete take place in the cement paste and the paste/ aggregate boundaries, the attack of the alkali-minerals (water/ pore solution) and the release of alkalis will be influenced	

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34	- supply of NaOH (boosting) will accelerate the release of alkalis from aggregates due to the increased attack of the alkali-minerals at high pH - the type of alkali ions (Na^+ or K^+) and the source (e.g. de-icing salts) influence the release of the alkalis - boosting could initiate mechanisms that probably will not appear in the field - boosting should not be an option for a performance-test	[5, 6, 7, 8]
35	- with increasing curing time, temperature and RH, the hydration degree will increase, hence the paste will become denser, and the release of alkalis could be aggravated during further testing *Question: Is this in contrast to point (2) in line 29,30 (see above)?*	
36	- insignificant	
37	- insignificant	
38	- insignificant	
39	- insignificant	

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Influence of mix/design casting on the composition of the concrete pore solution
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$Ca(OH)_2$		
Line number	**Question / hypothesis**	**Reference numbers**
29, 30	- with decreasing w/b-ratio the content of hydration products decreases and the hydration products tend to become more homogeneous and contain less crystalline hydrates (particularly portlandite) - at very low w/b some of the portlandite may occur in nanometre dimensions rather than in well crystallized form - if the w/b-ratio is similar in laboratory and field, there will be less/no influence	[9, 10]
31	- insignificant	
32	- insignificant	
33	- higher binder (cement) content means more C_3S/C_2S in the concrete and consequently a greater portion of $Ca(OH)_2$ will be formed	
34	- $Ca(OH)_2$ plays an important role for ASR: it is necessary for producing swelling gels and it is a buffer to maintain a high hydroxide concentration in the pore solution - in alkali hydroxide solutions, the solubility of $Ca(OH)_2$ is decreased, what supposes that alkali boosting by NaOH may influence/change the ASR mechanisms compared to field concretes - the ASR mechanisms in the field induced by externally supplied alkalis is different and involves $Ca(OH)_2$ as well. E.g. will alkali-acetates/-formates increase the solubility of $Ca(OH)_2$) - simple boosting with NaOH to compensate leaching or to accelerate ASR will influence/change the chemical conditions in the concrete, and, depending on the type of alkalis added, can change the "nature" of the ASR - boosting should not be an option for a performance-test	[11, 12, 13, 14]
35	- high temperatures during curing will accelerate the formation of $Ca(OH)_2$ and decrease its solubility - with increasing temperature, the crystal size of $Ca(OH)_2$ decreases, what could influence its solubility kinetics	[9]

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Influence of mix/design casting on the composition of the concrete pore solution

36	- insignificant	
37	- insignificant	
38	- e.g. superplasticizers help to disperse cement particles, consequently hydration products as $Ca(OH)_2$ are dispersed more homogeneously throughout the paste - Do such effects have a significant influence on lab/field correlation? - finally: in a performance-test, the same chemical admixtures as used in the field should be used	[15]
39	- insignificant	

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Influence of mix/design casting on the composition of the concrete pore solution
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OH^-		
Line number	**Question / hypothesis**	**Reference numbers**
29, 30	- with decreasing w/c ratio the OH^- concentration in the pore solution increases and vice versa - if the w/b-ratio is similar in laboratory and field, there will be less/no influence	[16]
31	- insignificant	
32	- insignificant	
33	- higher binder (cement) content means more alkalis and a greater portion of $Ca(OH)_2$ are available, consequently there is a greater depot of OH^-	
34	- alkali boosting (NaOH) will increase the OH^- concentration	[17]
35	- insignificant	
36	- insignificant	
37	- insignificant	
38	- insignificant	
39	- insignificant	

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Influence of mix/design casting on the composition of the concrete pore solution
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Alkali content		
Line number	**Question / hypothesis**	**Reference numbers**
29, 30	- if the binder (cement) content is kept constant, there will be no influence	
31	- insignificant	
32	- insignificant	
33	- the alkali content increases with increasing cement content - but: if the binder content for the performance-test is the same as for the job mixture, there will be no influence	
34	- alkali boosting increases the alkali content - the type of alkalis added (Na, K / hydroxides etc.) will influence/change the chemical conditions in the concrete and can change the "nature" of the ASR and the type of formed ASR-gels - the K/Na ratio used might be important too, because different gel composition result in different expansion behaviour	[18, 19]
35	- insignificant	
36	- insignificant	
37	- insignificant	
38	- some chemical admixtures have a considerably high alkali content, but the added amounts are mostly low - in a performance-test, the same chemical admixtures as used in the field should be used	
39	- insignificant	

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Influence of storage conditions on the properties of hydration products formed

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1 Introduction

In a given concrete containing reactive aggregates the reaction potential of a damaging alkali-silica reaction is influenced to a great extent by the composition of the pore solution with its function as a reaction partner for the reactive silica and as a supplier of moisture. Its alkali concentration is determined primarily by the cement composition and by the dissolving and fixation reactions with their mutual interaction. Therefore, the influence of parameters of storage conditions during testing, such as temperature and the time and durations of different climate conditions is analysed concerning its influence on the properties of reaction products formed by Portland cement (OPC), ground granulated blastfurnace slag (GGBS), fly ash (PFA) and silica fume (SF). This survey focuses on the impact of these parameters on the alkali binding capacity of the reaction products and thereby on the alkalinity of the pore solution. The influence of storage conditions on reaction products of meta kaolin, fillers, lithium salts and other SCMs were neglected because these are of minor practical importance.

2 Questions and literature survey

2.1 How does the temperature influence the alkali binding capacity of hydration products formed with OPC, GGBS, PFA and SF and how do these products influence thereby the alkalinity of the pore solution? (J-M 1-2)

The level of expansion of concrete containing reactive aggregate depends on the reactivity of the aggregate and the alkali content of the pore solution of the concrete. Therefore, it is important to know which phases can release alkalis to the pore solution, which reaction products are able to bind them and how the binding capacity of reaction products is influenced by different storage conditions.

CSH phases

The propensity of the CSH phases to bind alkalis varies with their stoichiometric composition. In the pozzolanic and latent hydraulic reactions, CSH phases are formed which have a lower lime content than their counterparts in Portland cement. In general, the assumption is that the binding of alkali to these phases will be increased /Bha79, Ray82, Tay85, Tho91, Uch87/. Beyond that, the binding capacity increases with increasing alkali content of the pore solution and with an increasing amount of CSH phases /Sch04/. At temperatures up to about 100°C practically the same CSH phases are formed as at normal temperatures, but the degree of condensation of the CSH phases is greater the higher the temperature and the lower the amount of moisture available during the hydration in the cement paste /Loc05/. With an increasing condensation degree of the silicate anions in the CSH phases the Ca/Si ratio decreases /Loc05/. Thus the binding capacity of CSH phases increases with increasing temperatures. At high condensation degrees of the silica more $[SiO_4]^{4-}$ tetrahedra are linked to another by shared oxygen atoms.

Ground granulated blastfurnace slag (GGBS)

GGBS can release alkalis to the pore solution /Sch04/. The extent is much less than that of clinker and is almost independent on the alkali content of the GGBS /Sch04/. The alkalinity of the pore solution of GGBS containing cements is mainly attributed to the reduced clinker content of the cement /Sch04/. In cements with GGBS alkalis are mainly adsorbed by the CSH phases. Up to 40 % GGBS the Ca/Si ratio of the CSH phases and therefore also the sorption properties are similar to that of OPC /Sch04/. Higher temperatures may lead to a higher condensation degree of the silica in the CSH phases and therefore to a lower Ca/Si ratio /Loc05/. Thus the formed CSH phases can adsorb more alkalis.

Fly ash (PFA)

The efficiency of a given level of fly ash to reduce the alkalinity of the pore solution seems to depend mainly on its calcium, alkali and silica content /She00/. In PFA containing cements the alkali fixation in the resulting reaction products starts at the same time as the pozzolanic reaction after a period of 28 days which results in a successive reduction of the dissolved alkali content. PFA reduces the pore solution alkalinity beyond just dilution /Sch04/. Due to the pozzolanic reaction the CSH phases are low in calcium and have a high alkali binding capacity.

More reaction products of fly ash are formed at 40°C and 60°C than at 8°C and 20°C so that more alkali can be bound /Bae09/. The average Ca/Si ratio increases with increasing reaction time and increasing temperature, which results in a decreased alkali sorption capacity. There is no difference in reaction degree between 40°C and 60°C whereas the Ca/Si ratio is higher at 60°C, which results in a decreased binding capacity. So the temperature is affecting two opposing trends that influence the amount of bound alkalis: the amount of reaction products and their Ca/Si ratio. Apparently there is an optimum temperature for the highest binding capacity. This is confirmed by pore solution analyses. It was found that the alkali concentration in the pore solution was mostly the lowest at 40°C /Bae09/.

Furthermore PFA can react to alkali-incorporating zeolite-like products. These products are supposed to be metastable and can react in the presence of calcium to CSH, CASH or CAH phases /Sch04/. Whether this reaction results in an increase of the alkali content in the pore solution depends on the amount and the stoichiometric composition of the resulting reaction products. It is assumed that some of the alkali-incorporating zeolite-like products remain because the availability of calcium due to the slow diffusion through the dense pore network is poor. There is little information on the binding capacity of CAH and CASH phases and how their capacity is influenced by temperature changes.

Silica fume (SF)

Silica fume reacts fast with the alkalis from the pore solution to an alkali-silica-gel /She02/. Thus the alkali concentration in the pore solution decreases within the first two days of hydration /Sch04/. The gel at the border of the silica grain reacts with available calcium to CSH phases that have a low Ca/Si ratio and a high alkali binding capacity. Alkalis will be released by this reaction. Most alkalis are bound by the alkali-silica-gel in the silica fume particles and the additional low calcium CSH phases. But as long as alkali-silica-gel exists inside the particle it is driven to react with calcium. Alkalis will continuously be released into the pore solution and increase the alkalinity of the pore solution after 28 days up to 2 or 3 years /She02/. This means that after a fixation phase at least parts of the alkalis become available again for an alkali-silica reaction.

2.2 Does the concrete's age when exposed to a special climate influence the hydration products formed with OPC, GGBS, PFA and SF? (J-M 10)

To access the alkali reactivity potential of specific aggregates or concrete compositions in a relatively short time, mortar or concrete samples are exposed in many tests to high temperatures at very early ages. In /Bok08/ it is assumed that an ASR takes place within 28 d to 56 d, when maximum alkalinity in the pore solution usually is achieved. Under normal conditions (20°C) the pozzolanic reaction of PFA starts after the age of 28 days /Sch04/. If the concrete with PFA is exposed to high temperatures at an early age, alkalis may be bound by the accelerated pozzolanic reaction that takes place before the ASR. This results in a pore solution, which has a lower alkalihydroxid content when the ASR starts. To reduce this impact on the alkalinity of the pore solution it is recommended to store the concrete samples under normal temperatures to allow a normal development of pore solution composition. This is confirmed in /Hei08/, where the accelerated concrete prism test at 60°C is extended by a pre-storage period of 28 and 90 days at 20°C before the samples are tested at 60°C.

2.3 Does the humidity influence the properties of hydration products formed with OPC, GGBS, PFA and SF? (J-M 4-6)

Humidity is necessary to ensure a high degree of hydration. It is assumed that water is always supplied sufficiently during testing by storage above water, submerged in water or in aqueous solutions with and without alkalis.

2.4 How do external alkalis influence the reaction products formed with OPC, GGBS, PFA and SF? (J-M 6 and 11)

Several studies have shown that alkalis from external sources, e. g. NaCl from de-icing salts increase expansion of mortar or concrete that contains reactive aggregates /Cha87, Kaw88, Sib98/. According to /Nix86/ the introduction of sodium chloride to a cement paste, mortar or concrete at the mixing stage results in an elevation of the hydroxyl ion concentration of the pore solution to a level similar to that produced by a Portland cement with an equivalent alkali level. This will increase the likelihood of a damaging ASR in concrete with alkali-reactive aggregates. According to /Cha86/ free $Ca(OH)_2$ promote Na^+ ions from the NaCl solution and OH^- ions from $Ca(OH)_2$ together with H_2O molecules to penetrate in a reactive grain. From /Cha05/ can be derived that neutral alkali salts like NaCl may accelerate an ASR by increasing the ionic strength of the pore solution. Information on the influence of external alkalis on the alkali binding capacity of the reaction products formed with OPC, GGBS, PFA and SF was not found.

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Influence of mix design/casting on the properties of hydration products formed

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Firstly, it must be recognized that there exists a difference between the properties of the reaction products and the properties of a hardened concrete. The table in the end of this Appendix (being part of the table in Appendix 1B) shows the relative importance of some parameters (water/binder ratio, air content, aggregate moisture content, binder content, alkali boosting, curing, type of end studs, form oil and admixture type incl. Lithium) on the properties of the formed hydration products by using different binders and additions; CEM I cement, silica fume, pulverized fly ash, slag, meta kaolin, other SCM's and fillers.

The importance of splitting the water/binder ratio into two parts, namely the diffusion properties (open porosity: the pores accessible from the outside of the specimen) and the porosity (total porosity: this includes also the closed pores with no connection with the outside of the specimen [1, 2]) was not clear, and thus this was considered as only one parameter: the water/binder ratio.

Of the parameters mentioned before, some of them are not important in this study. This implicates that all the values in that row can be considered to have no significant importance, thus given value 0 in the table. The rows implemented herein are the air content, the type of end studs and the type of form oil. Nevertheless, it must be mentioned that these parameters may have an effect on for example the properties of the hardened concrete [3] (compression strength is reduced with increasing air content [4]). A recent experiment in our laboratory (an accelerated alkali silica reaction test [5]) showed that if one used more form oil for making the samples, a different behavior of the hardened samples towards the mentioned reaction was obtained. This effect could be designated to the changed superficial properties. Also the aggregate moisture content belongs to this group, because this is normally recalculated in the water/binder ratio, which implies that this factor may not have an effect.

Two different types of fillers exist: reactive - and non-reactive fillers [6]. Non-reactive fillers are not participating in the hydration reaction, which implies that they will not be influenced by any of the mix design / casting parameters mentioned in the past (i.e. value 0 in the "filler column". The reactive fillers will be discussed as part of the other columns (i.e. PFA, slag, …) [7]. Also the column with Lithium does not have much importance in this table, because the lithium has no hydraulicity, although it can influence the reaction kinetics [8, 9, 10].

The water/binder-ratio is, in relation with a CEM I cement, a very important factor for the properties of the hydration products formed [11]. If too little water is added to the concrete mix, other reaction products may be formed. It needs to be mentioned that for a normal concrete composition, i.e. water/binder ratio in the range 0.4 and 0.5, the hydration products will not be much different. It might be possible that the Ca/Si-ratio (C/S-ratio) in the C-S-H phases (from C-S-H I which is 0.8 to C-S-H II which is 1.5) is changed by varying the water/binder factor. Nevertheless, the reaction kinetics of the hydration reactions and the obtained structure of the material (concrete) may change. The use of another water/binder-ratio implicates a different alkali concentration (by extraction), which leads to a different behavior and may result chemically in other reaction products or a different physio-mechanical behavior of the product.

Other materials can be used to decrease the amount of Portland clinker. With each of these materials, a k-factor is coupled [12]. When using silica fume, this will also react and thus be influenced by the water/binder factor [6, 13]. However, it must be mentioned that silica fume has a very high specific surface and thus retains a great part of the water that cannot be used for hydration anymore, while on the other hand it increases the resistance by performing the role of "lime". Similarly for the fly ashes [13, 14] and the slag [2, 15], which reacts at much later ages compared to silica fume, and which can inhibit alkali silica reactions (e.g. about 20% pulverized fly ash is needed to avoid alkali silica reaction, which is twice as good as when using slag at that percentage).

About the importance of meta kaolin (a fritted form of kaolin at about 1200°C), discussions may exists, because some researchers say it forms reaction products, while others are not in accordance with them [16, 17, 18]. Also other cementitious materials (e.g. natural pozzolanic materials [19]), that will react with water (and eventually other reagentia), may be important for the properties of the hydration products formed.

The binder content in the concrete, in the meaning of content of cementitious paste, is not assumed to significantly influence the properties of the hydration products formed.

It's well known that the temperature during curing influences the reaction kinetics and indirectly the reaction products. All hydration products, by definition, are also influenced by the curing moisture and time. [3]

The admixture type may also be a very important parameter. Mostly they influence the behavior of the material in a non-solid state, like for example fluidity, the need for water to be workable, … [20]. They may although have an effect on the reaction products that are formed, due to reaction kinetics (for example parallel non-reversible reactions or the blocking of other reactions by selectively changing the reaction kinetics), adsorption of the admixture molecules on surfaces of hydrated (or at that moment still not reacted) cement particles. The type of admixture is assumed to be most important when CEM I is the binder. However, also when other materials that can hydrate are used, it may be important. [11, 21, 22, 23]

"Boosting" the alkali level by addition of alkalis to the mixture will have an effect on the reaction products [24, 25, 26]. For example, if the alkali concentration is increased, this will have an effect on the formed ettringite by influencing its stability, shape, … [27, 28]. This will change the hydration kinetics as the hydrated structures are formed during the reaction. Also for the other cementitious materials, this effect may take place.

CRIC have carried out a study to determine the upper limits of Na_2O_{eq} allowed for a large amount of Belgian cements. The maximum Na_2O_{eq} established levels (% in cement mass) enable to define a Low Alkali class ("LA") in the Belgian norm [32]: CEM I (0.6 %), CEM III/A (0.9 and 1.1 % for slags respectively < 50 % and ≥ 50 %), CEM III/B (1.3 %), CEM III/C (2.0 %) and finally CEM V/A (1.5 %). This work was done by the known technique of "doping" concretes, made with a reference reactive aggregate, with different alkalis levels. M. Böhm has shown that boosting a concrete with alkalis is not equivalent to a "natural" alkali content [29]. A. Leemann has also questioned the Na_2O equivalent concept, i.e. the relation between Sodium and Potassium [30]. However, even new de-icers, potassium or sodium acetates, used for highways or air field pavements may generate AAR [31].

Implementing these results in a table of importance (0: not important, 1: a bit, 2: a bit more, 3: very important), gives the following results.

			CEM I	Silica fume	PFA	Slag	Meta kaolin	Other SCMs	Fillers…	Lithium
Mix design/casting	Water/binder ratio	Diffusion properties Porosity	3	1	1	1	2	1	0	0
	Air content	Porosity	0	0	0	0	0	0	0	0
	Aggregate moisture content		0	0	0	0	0	0	0	0
	Binder content		0-1	1	1	1	2	1	0	0
	Alkali boosting	NaOH	3	1	1	2	0	0	0	0
	Curing	Temp./moisture/time	3	3	3	3	3	2	0	0
	Type of end studs		0	0	0	0	0	0	0	0
	Form oil		0	0	0	0	0	0	0	0
	Admixture type		2	1	1	1	1	1	0	0

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Influence of storage conditions and aggregate type on the aggregate reactivity
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Influence of storage conditions on aggregate reactivity

Line number	Parameter	Question	Influence	Reference number
1	Temperature – Curing	*Does the curing temperature influence the reactivity of aggregates and the expansion of the specimens?* - Very small number of references. [14] refers a modification of the NBRI accelerated test and concluded that there is no significant effect.	0	[16]
2	Temperature - Exposure	*Does the environmental temperature influence the reactivity of aggregates?* - In literature about microbar tests, NBRI test and autoclave test it is concluded that high temperature in storage can induce higher degree of reaction and higher expansion. - However, [18] studied concrete prism test and accelerated concrete prism test and verified that the expansion was considerably lower for the accelerated test (60ºC), probably due to alkali leaching (higher concentration of Na and K in the water at the bottom of the container) and changing in pore solution composition (higher sulphate due to solubility of ettringite and lower hydroxyl), with decreasing of pH and lower solubility of quartz. Higher expansion occurs at higher temperature just in early-age. There is a good correlation between CPT38ºC and CPT60ºC. - AMBT – conditions are considered too severe for some aggregates. - Concerning the pore solution, increase in temperature leads to an increase of sulphates and decrease of hydroxyl ions. - [50] refers that CPT is the test that shows best correlation with filed structures (also highlights petrography). - Tests with Brazilian aggregates showed a good correlation between CPT38ºC, CPT60ºC and between CPT and field performance [51]. AMBT fails to identify reactivity of granite-gneiss and quartzite (reactive in field structures). - [53] shows that high temperature and humidity can decrease the likelihood for ASR in lab conditions compared to field performance. - [56] reports that by comparison of different tests concludes that from AMBT80ºC, CPT60ºC to CPT38ºC the number of aggregates classified as reactive decreases. Non-reactive sands can have reactive components which are activated for higher temperatures. CPT60ºC identifies slowly reactive rocks such as gneiss-granite.	3	[4], [16], [17], [18], [20], [50], [51], [53], [56], [57], [58], [59]

Line number	**Parameter**	**Question**	**Influence**	**Reference number**
(2)	(Temperature Exposure)	- [57] shows that higher temperature (60ºC) increases leaching, and as a result, CPT60ºC shows lower expansion than CPT38ºC. At high temperature, “non-reactive” aggregates influence results. - [58] performed field tests in 2 different locations to study the effect of temperature. Concluded that expansion is faster and higher for the place with higher temperature, but it depends on the aggregate selected. The difference in expansion increases with decreasing reactivity level. - Tests with higher temperature show that expansion starts faster but levels out quickly due to leaching. In the long term (1 year), expansion for 38ºC is greater than for 60ºC [59].		
3	Temperature - Measuring	*When measuring the expansion, does the temperature influence the results?* - Curing temperature is different for different tests. It is not easy to correlate results from different tests when there are other parameters involved (size of prisms, mortar/concrete composition, storage conditions). For each test, there should be maintained the same temperature for measuring, avoiding another variable in the system.	?	Not found
4	Humidity - Above water	*Is there a difference in results of expansion when samples are stored above water or submerged? Are there other factor influencing the results?* - The higher the humidity, the higher the expansion. However, results are not clear. - It seems that for concrete prism test, [43] found the expansion was stronger for the specimens stored in a sealed box over water. Prisms in moist room show the least expansion and the greatest leaching. Also say that mortar bars stored in containers without wicks or sealed in plastic bags have significant expansion. The reverse is verified for concrete prisms: the removal of wicks reduces the expansion considerably. - Immersion lowers expansion due to alkali leaching in small specimens	2	[6], [7], [43]
5	Humidity – Submerged			

Line number	Parameter	Question	Influence	Reference number
6	Humidity - With alkalis	*How does the presence of humidity influence the aggregate reactivity?* *Does the concentration of alkalis in the pore solution affect the expansion of the specimens?* - Different content of alkalis is used in different tests. For the same aggregate, the result might be “innocuous” or “reactive” depending on the content of alkalis available for reaction. - When alkalis are used in the immersion solution, the cement alkali content has no significant influence on mortar bar expansion. - For CPT, expansion increases with increasing alkali content in the system. Leaching of alkalis occurs specially with small specimens in the laboratory. Leaching leads to reduction of expansion rates. - Alkalis from other sources must be considered (blocks with low alkali content exposed outdoor showed AAR). - [40] concluded that alkalinity decreases in the pore solution during laboratory concrete prisms due to leaching at high moisture environment. Pore solutions in concrete structures are mostly not subject to leaching (exception e.g. dam galleries). - For tests at 40ºC, higher expansion occurred for higher alkalis [52]. Alkalis in pore solution are lower when GGBFS or FA is added (than with OPC). Expansion occurs when a critical value of pH is exceeded, but this depends on the type of aggregate (more reactive aggregates have lower critical value). Authors say the test might not reproduce long term behaviour. - Extreme humidity leads to dilution of the pore solution, but also to intensive leaching [53]. - In CPT 38ºC expansion increases with increasing alkali content in the system. Also for prisms with SF [54]. - Non-reactive sands can have reactive components which are activated for higher alkalis [56]. - Expansion in field tests is affected by addition of alkalis, but the effect varies with aggregate type [58]. In CPT 38ºC, the increase in alkalis leads to increased expansion. - Different aggregates have different critical alkali limit [62].	2	[19], [36], [40], [41], [44], [52], [53], [54], [56], [58]

Line number	Parameter	Question	Influence	Reference number
7	Wrapping/ Water amount added	*What is the effect of wrapping the samples?* *Is there a known effect related to the characteristics of the storage or use of wrapping?* - [45] refers a study using the ultra-accelerated concrete prism test (60º) with a reactor box and the wrapping method, and both methods yield similar expansion. AAR-4 test will prefer the reactor box.	2	[45]
8	Prism size	*Does the size of the prisms influence the expansion?* - Many authors worked in tests with different dimensions of the specimens, but in general no reference is made to the relation between the prisms size and the expansion. It is concluded by [1] that the larger the cross-section of a concrete prism, the greater the expansion due to leaching effect on the smaller specimens. - For CPT, when testing marginally reactive aggregates, larger specimens show higher expansion. Though they are slower at start, they continue to expand at a steady rate. When testing extremely reactive aggregates, smaller specimens expand more. - AMBT: it is difficult to compare results for different bar sizes and different aggregate types [50]. - [54] found some differences in field performance due to more exposure to humidity (dependent of exposed surface). - [62] showed that even with large concrete prisms, there is alkali leaching which cannot be neglected.	1	[1], [2], [4], [19] [20], [27], [50]

Line number	Parameter	Question	Influence	Reference number
9	Type of container / stable water level?	*Do the type of container and the water level influence the reactivity of aggregates?* - The type of container and the water label influence the leaching of alkalis, thus affecting the expansion of specimens. Bars stored in a container with and without wicks show different expansion which is greater without wicks. Wicks promote leaching of alkalis reducing the amount available for reaction and thus reducing expansion. However, for concrete prisms wicks are necessary to ensure sufficient moisture in the container, thus leading to higher expansion. - [18] refers companion sets of test prisms stored in different containers and concludes that the type of container has little influence on the expansion. - This parameter has to be analysed with line 7 and line 11 as the conditions are connected. **Issue to be resolved: alkali leaching.**	2	[6], [18], [23], [24], [42], [43]
10	Time	*How does the duration of the tests affect the expansion of specimens?* - Expansion of specimens increases as the treatment time increases. The behaviour is different for carbonates and terrigenous aggregates when compared with igneous and metamorphic rocks. - [51] states that slowly reactive aggregates are best assessed at 120 days (than with 90) for CPT60ºC (after 120 days the expansion stabilizes). - [54] reported that for concrete prisms with SF, expansion increases with increasing time and increasing alkalis in the mixture. - [62] showed that the weight of prisms increases with expansion and with time (after a slight weight loss in the first weeks for some of the concretes). If prisms show weight loss over time, this must be due to insufficient water in the system and low expansion will be recorded.	2	[11], [13], [32], [36], [51], [54], [62]
11	External alkalis	*Does the presence of external alkalis (solution in the container) influence the reactivity of aggregates?* - Expansion increases for higher concentration of alkalis in the solution and is also dependent on the salt used in the immersion solution (NaOH, NaCl or just RH). The greater the residual alkalis content, the greater the expansion. - Different aggregates react in a different way when exposed to salt solutions. - [32] found that the expansion increased and then decreased, concluding that there was a “pessimum” effect for external alkalis.	1	[4], [6], [32], [43]

Issue to be resolved: aggregates that pass the mortar bar test, but fail the concrete prism test *(ex. some granites/granitic gneiss)*

Influence of aggregate type on aggregate reactivity

Line number	Parameter	Question	Influence	Reference number
12	Slowly reactive; grading/size distribution	*Do the size and/or the grading of slowly reactive aggregates influence the aggregate reactivity?* - The influence of aggregate size and grading on AAR depends on the nature and composition of the aggregate. - Features associated with AAR seem to be different for fine aggregates and coarse aggregates of a specific composition. - Also depends on the type of test and the test conditions. Texture of the aggregate should be studied. - [61] showed that tests using smaller grains of aggregate are more sensitive to denser aggregates such as tuffs and gneisses. Large particles of porous aggregates seem to cause larger expansion than smaller porous aggregates. AMBT seems to be sensitive to more porous aggregates but not suitable to evaluate reactivity of sands with many quartz crystals.	1	[14], [38], [61]
13	Slowly reactive; mineralogy	*Does the composition of slowly reactive aggregates influence the aggregate reactivity?* - There are reports from field concrete about AAR and gel formation associated with slowly reactive aggregates. Accelerated laboratory tests do not detect the reactivity of these aggregates. Texture is more important than mineralogy.	1	[14]
14	Fast reactive; grading/size distribution (Fast reactive; grading/size distribution)	*Do the size and/or the grading of fast reactive aggregates influence the aggregate reactivity?* - The size of reactive aggregates influences the reactivity. Reactivity is stronger for intermediate sizes or larger particles, depending on the composition/texture of the aggregate. - Angularity seems to be important for intermediate sizes (crushed rocks react more than natural sands). - Other aggregates show stronger AAR for smaller particles. Larger particles react slowly but reaction maintains longer. - The use of small particles in texts leads to lower expansion because the original micro-texture of the rock is lost during sample preparation (so expansivity is better evaluated with CPT than mortar bar tests) [36]. - [50] refers that coarse aggregates lead to more damage than fine fraction in Norwegian guidelines test AMBT. CPT test is capable of taking into account the effect of different reactivity of different grain sizes. - [60] verified that for Pittsburg limestone have different performance in mortar bar and concrete prisms, due to size of particles used (expansion is lower for mortar bar).	1	[36], [37], [39], [47] [49], [50], [60]

Line number	Parameter	Question	Influence	Reference number
15	Fast reactive; Mineralogy	*Does the composition of fast reactive aggregates influence the aggregate reactivity?* - Mineralogy can influence the reactivity but texture is more important. - More reactive aggregates expand more than low reactive aggregates. - ASR products generate more water absorption in reactive than in non-reactive concrete samples. - [55] used reactive aggregates and the sedimentary ones show higher expansion in microbar tests. This is due to dissolution of the grains of granite and gneiss. But both aggregates show expansion in microbar test. Found contradictory results for CPT and microbar. CPT correlates better with field performance. - [62] showed that expansion rates are higher in the first years (0,5-3 years) and then decrease or flatten out. They decrease earlier for the most alkali reactive mixes.	1	[4], [14], [19], [33], [62]
16	Pessimum? grading/size	*Do the size and/or the grading of pessimum content reactive aggregates influence the aggregate reactivity?* - All the sizes show strong reactivity, though the larger react slower and in a gradual way. Generally reactivity increases with decreasing of size grain.	1	[13], [22], [47]
17	Pessimum? Mineralogy	*Does the composition of pessimum content reactive aggregates influence the aggregate reactivity?* - [12] tested opal grains and found that residual materials were neither uniformly low Ca gel or high Ca gel, but content varied from one grain to the other. - [44] tested opal by mortar bar tests, and concluded that the larger expansion corresponds to the pessimum content of the aggregate. - More reactive aggregates show maximum reactivity for lower percentages. - Laboratory tests permit the identification of pessimum content. - Field damage is proportional to the content of reactive aggregate.	1	[3], [12], [22], [28], [44]
18	NR-reference/ non-reactive?	*Is the classification of non-reactive universal?* - Non-reactive aggregates can affect the expansion by contributing with additional alkalis. There is expansion with non-reactive natural sands, meaning that reaction occurs. - Limestone can contribute with calcium to the gel. - Conclusions about the non-reactivity depend on the test performed, and sometimes the results do not agree with field performance. - Tests performed with different non-reactive aggregates mixed with a specific reactive aggregate show different results. Natural non-reactive sands show stronger reactivity than manufactured or crushed sands. - [57]: Higher temperature (60ºC) increases leaching. At high temperature “non-reactive” aggregates influence results. For the CPT38ºC there is reduction on expansion dependent on the non-reactive aggregate selected. - [59]: Use of different non-reactive sand gave different multi-laboratory variation for test results.	1	[3], [26], [35], [57], [59]

Line number	Parameter	Question	Influence	Reference number
19	Water absorption	*Do the porosity and permeability characteristics of aggregates influence the reactivity of the aggregate?* - Aggregates with higher porosity show higher reactivity because the access to pore fluids is easier. - [53]: Tests performed with different exposure to water show that concrete pore solution is diluted by water uptake when stored in fog chamber (when compared to storage above water or above satured solutions). The absorption is not dependent on cement type.	1	[3], [4], [10], [14], [26], [53]
20	Filler type	*Is there any relationship between the presence/composition of filler and the reactivity of an aggregate?* - The presence of filler decreases the concentration of alkalis in pore solution and of reactive aggregates, thus the reaction can decrease independently of the reactivity of the aggregate. - Some Ca is necessary for the formation of gel. Otherwise silica dissolves in high alkali solution. - [6]: To prevent or minimize AAR a sufficient amount of cement should be replaced by supplementary cementing materials. - [9]: FA reduces the expansion due to ASR in concrete immersed in alkaline salt solution. Silica particles can be removed by dissolution without associated damage. The addition of $Ca(OH)_2$ promotes expansion in FA concrete. In the absence of Ca rim, the high Na gel can disperse through the pore structure alleviating internal stresses. - [50] refers that AMBT predicts effect of reactive rock fillers to inhibit expansion due to ASR, in contradiction to CPT, but the test of non-reactive limestone filler gave no effect. Conclusion: methods using very high temperature (e.g. AMBT) should not be used to evaluate the fillers containing silica. - [52]: CPT(40ºC) tests with GGBFS and FA show lower expansion. - [53]: Lab tests using SCM avoid deleterious ASR when compared with field performance, probably because at high T and RH viscosity of gel decreases. Also, with slowly reactive aggregates, SF reacts quicker and can inhibit ASR for higher temperature, but needs dilution of the pore solution. With fast reactive aggregates, ASR starts parallel to the pozzolanic reaction and prisms show no significant expansion during lab tests. - [54]: The use of FA resulted in reduction of expansion for all aggregates. With SF expansion increases with increasing time and increasing alkalis in the mixture. - [60]: The use of FA, slag and Li suppress the ASR expansion both in lab tests and in field conditions for some aggregates (e.g Spratt), but not all (e.g. Pittsburg). - [62] reports that different fillers show different expansion. ***Issue to resolve: does filler contribute/prevent AAR?***	1	[5], [6], [9], [12], [38], [48], [50], [53]

References: See appendix 6.2

Effects of the testing conditions on the Alkali Aggregate Reaction products

Topic: Does the testing condition affect reaction products formed during AAR? Comparison with field AAR reaction products.

It seems that very few authors have published papers on this specific topic. Some have compared reaction products coming from field concretes to lab mortar manufactured with the same aggregates but using a single accelerated test, rarely with two of them. Apparently nobody tried to compare reaction products coming from various kinds of accelerated tests samples performed on the same sets of aggregates.

Among the rare existing papers, the most interesting is probably that of Gravrilenko et al. **[1]** who compared concrete taken from Spanish dams (drill cores) and mortar bars made up with the same aggregates (crushed granitic mylonite and quartzite) and tested according to the ASTM C-1260 testing procedure (water:cement of 0.47, bars 25.4x25.4x287 mm^3 cured 24 h in wet chamber at 20°C and then at 80°C for 24 h, bars are then subjected to treatment with a 1N NaOH solution at 80°C for 14 and 28 days). This testing procedure is very close to the NBRI testing method. After testing, mortar bars and concrete cores were both studied by scanning electron microscopy. In both cases they found **large varieties of gel: compact smooth gel, lepispheres and sheet sponge or clot morphology**. Even if this accelerated testing procedure does not seem to give rise to specific reaction product morphologies, **they found a very different chemical composition between field and lab reaction products**. Gels formed in mortars (with alkali-boosted cement) were highly enriched in Na and poor in Ca, with often more silica than in the field concretes. Besides, they noticed that contrary to the field concretes, in mortar the closer the gel is from the cement paste, the richer in sodium it is.

Decades earlier G. Davies, R.E Oberholster **[2]** had compared alkali-silica products formed in field concretes with those formed during the NBRI test. They had showed that, compared to the field, **NBRI test accelerates the reaction but does not modify the naturally occurring process**. Nevertheless they had noticed **fluid gels exuding into the NaOH solution**, under the form of thin filaments, during the test. SEM examinations of gel done at the completion of the test revealed that **morphologies very similar to those found in field concretes [3] irrespective of whether NAOH or KOH solutions are used (massive gels, sponge-like texture and rosette-like phase).** By washing gels with distilled water, they both drastically reduced gel alkali content and Ca/Si ratio. They have drawn from this result that alkali ions present in the **gels are likely absorbed rather than chemically bound.**

Later Zidzislawa **[4]** compared alkali-silica reaction products formed during a **conventional test** (long lasting test) **and an accelerated test**. He started from 25x25x285 mm^3 mortar bars, with W/C of 0.47, but using cement alkali-boosted with K_2SO_4 instead of NaOH so as to get 0.35 to 1.10% Na_2O_{eq}. Half of the bars were stored at **38°C and 95% RH**. The other half was immerged after curing into a 1N NaOH solution at 80°C (**NBRI testing procedure**). For the latter, expansion measurements were taken every 2 days, over a period of 14 days. This researcher chose K_2SO_4 to get more realistic pore solution knowing that most cements contain more potassium than sodium. SEM observations of mortar stored for 30 months at 38°C or 14 days in 1N NaOH solution at 80°C showed **the same ASR-gel morphology, but large quantities of massive**

ettringite were found in cracks, around some aggregates and in air voids only for the first set of prisms. No ettringite was found (for not stable) in the second case. According to this author, this **secondary ettringite formation can play a considerable role on expansion**, hence **higher expansion was found with the 38°C storage than with the accelerated testing** (around 0.65% versus 0.11%). He assessed too that **addition of potassium in the sodium-potassium silicate gel increases its viscosity and swelling properties.** On the other hand, he derived from his own test results that alkali content in cement considerably affects linear changes in the accelerated expansion test.

Conversely, Powers and Steinour **[5],** followed by other researchers showed that **sodium-rich gel tends to give greater expansions than potassium or calcium-rich gel** explaining this phenomenon with the double-layer theory.

Nevertheless, Kawamura and Iwahori **[6]** saw that pressure exercised under restraint is **higher with Ca-rich gel than with alkali-rich gel** (this restraint being minimised in thin mortar bars). In field concretes, alkali content is often limited, while calcium is continuously brought via the pore solution thanks to portlandite dissolution. **So in the field, ASR-related expansion can be both more intense and faster** (but its speed slows down with time). In lab mortar bars the **high level of sodium content** (brought from the NaOH enrichment of the mixing water or during alkaline curing) **leads to increasingly sodium-rich gel and probably artificially raises the silica-dissolution rate of some aggregates.**

Kawamura and al. pointed out also that **viscosity of low Na_2O/SiO_2 gels is much higher than high Na_2O/SiO_2 gel so viscosity of alkali-rich gels in mortars must be so low that they could not exhibit high expansive pressure.** This low viscosity leads to **exudation of great amounts of gel on surfaces of bars with alkali content higher than 2%**. **This exudation limits gel content inside mortar and by then possible expansion.**

L.J. Struble and S. Diamond **[7]** measured swelling properties of alkali silica gels of various Na_2O / SiO_2 ratio. Under “free-swelling conditions” they recorded swelling ranging from 0.1 MPa to almost 11 MPa, **gels with Na_2O / SiO_2 ratio of 0.33 and less exhibiting the lowest swelling pressures.** They found that the presence of calcium in the gel does not noticeably reduce either its swelling or its pressure-developing ability.

Chatterji **[8]** remarks that interaction of OH- ions with silanol groups existing on the silica or silicate-grains drastically increase their negative surface charges density. Thus, charge density rises with increasing pH and ionic strength of the pore solution. **NaOH contributes much more than Ca ions to pH and ionic strength.** Besides, NaOH decreases the Ca ions concentration in pore solution by the common ion effect. On the other hand, any pH rise depressed Ca ions concentration in solution, thus liberation and diffusion of silica are enhanced.

To sum up, **it seems that accelerated tests do no not significantly change AAR products compared to field concretes.** Nevertheless, tests carry out at medium temperature (less than 60°C) could lead to **secondary ettringite formation which contributes to the global concrete expansion**. Ettringite does not form or is unstable at higher temperature (roughly 65 to 70°C). Sodium enrichment gives rise to **low viscosity alkali-rich gels which can exude out of concrete, reducing internal pressure and expansion. On the other hand, alkali raises pH and by then silica dissolution and possible gel expansion.**

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Influence of storage conditions on gel "properties" (expansion)

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Influence of storage conditions on gel "properties" (expansion)

Line number	Parameter	Question	Influence	Reference number
1	Temperature; Curing	*Does the curing temperature influence the properties of gel?*	?	Not found
2	Temperature; Exposure	*Does the environmental temperature influence the properties of gel?* - Some of the products formed during laboratory tests are similar to those formed in field concrete. - Concerning the temperature in laboratory tests, greater amounts of gel are formed for higher temperature. Higher temperature tests resulted in greater amounts of Ca in the composition of gel, which according some authors is a prerequisite for the formation of expansive gel. - [53]: Viscosity of the gel decreases when temperature increases (lab tests) and maximum expansion decreases.	1	[17], [29], [21], [53]
3	Temperature; Measuring	*Does the temperature of the measures influence the properties pf gel formed?* - Probably.	0	Not found
4	Humidity; Above water	*Is there a difference in gel properties when samples are store above water or submerged?* - The quantity of gel is far inferior when there is no external water supply and there are nearly no products formation when specimens are dry. - For specimens stored in high humidity, it was observed that when immersed they absorbed a large quantity of water. - If chemical reactions and swelling are stopped due the lack of water, they can be reactivated quickly when water comes back. - Expansion of concrete with non-reactive aggregates is slower that with reactive aggregates.	1	[33]
5	Humidity; Submerged			

Line number	Parameter	Question	Influence	Reference number
6	Humidity; With alkalis	*Does the presence of humidity and alkalis influence the properties of gel?* - AAR happens if enough humidity and alkalis are available for reaction. Higher content of alkalis in the mix leads to high degree of reaction and greater expansion. - The more water, the more severe the degradation. Water increases concrete exchange when it is available during the formation of ASR products. After completion of the reactions, any added water will not cause extra expansion. Water exchanges are the same for reactive and non-reactive aggregates. - [30]: Alkali-rich mortars originate alkali-rich ASR gel. In case these gels produce great expansion in lab tests, in concrete members under restraint the expansive pressure may not be significant (great expansion but probably no damage in concrete structures). - [53]: Humid conditions decrease the likelihood for ASR.	1	[8], [17], [30], [33]
7	Wrapping; Water amount added	*What is the effect of wrapping the samples on the properties of gel?* - Wrapping gives less expansion than specimens without wrapping.	1	[33]
8	Prism size	*Does the size of the prisms influence the properties of gel?* - Very unlikely.	?	Not found
9	Type of container; stable water level?	*Do the type of container and the water level influence the properties of gel?*	?	Not found
10	Time	*Does the duration of the tests influence the properties of gel?* - Expansion increases on increasing the duration of the test for reactive aggregates but for non-reactive aggregates time has no effect.	1	[17], [37]
11	External alkalis	D*oes the presence of external alkalis influence the properties of gel?* - Testing specimens with different solutions permitted to conclude that the products formed differ in thickness and in composition. NaOH showed the strongest attack but KOH produced more crystalline gel. The dissolution of silica also varies with the compound in the solution but the amount of dissolved silica tends to be independent from the composition of the alkalis over time. Also there is little difference in the composition of the gel formed in mortar immersed in NaOH with or without calcium. - The increase in the alkali content in ASR gel in mortars decreases the expansion. The Ca content in ASR does not influence the expansivity of gel as the alkali content.	1	[29], [34], [37], [44]

References: See Appendix 6.2

Influence of aggregate type on ASR-gel formed during the exposure

Line number	**Parameter**	**Question**	**Influ-ence**	**Reference number**
12	Slowly reactive; grading /size distribution	*Do the size and/or the grading of slowly reactive aggregates influence the formation of gel? What about the quantity of gel formed?* - Aggregate size and grading influences the AAR expansion, depending on the nature, texture and composition of the aggregate and also on the type of test. - The presence of alkali-carbonate reactive rocks should be considered, as they can influence results. - The grain size can influence the quantity of gel formed, considering that small grains are substituted by gel, in general without calcium in the composition.	2	[14], [31], [38]
13	Slowly reactive; mineralogy	*Does the composition of slowly reactive aggregates influence the formation of gel?* - There are reports from field concrete about AAR and gel formation associated with slowly reactive aggregates. Some laboratory tests do not detect the reactivity of these aggregates. - Texture is more important than mineralogy. - The presence of limestone can contribute with Ca for the gel [3]. - [14] and [15] have analyses by EDS from gel in concretes with different composition of aggregates and didn't find difference in the composition of the gel.	1	[3], [14], [15]

14	Fast reactive; grading/size distribution	*Do the size and/or the grading of fast reactive aggregates influence the formation of gel?*
		What about the quantity of gel formed?
		- Opinions are different according to different authors:
		  - The larger the size of the aggregate particles, the higher the expansion.
		  - Larger expansion occurs for medium sized or low sized particles.
		  - Larger particles lead to smaller expansion at early ages but increase continuously at later ages.
		  - The effect of size on AAR is more pronounced in crushed aggregates.
		- The use of very fine aggregates destroys the original microstructure characteristic of the rocks (e.g. granites), underestimating the alkali reactivity of the rocks in the accelerated tests (e.g. size used in AMBT and Chinese autoclave method).
		- AMBT fails to recognise the non-reactive character of some aggregates (based on field performance) while failing to identify some other aggregates that are reactive in CPT. Better correlation with CPT is got with sizes: 1.25-2.50 and 2.50-5.00 mm.
		- Fast reactive aggregates show substitution by gel when in the fine fraction, mainly with no expansion associated. Coarse particles show cracks and expansion.
		- [36] found calcium rich AAR product formed around fine quartz particles due to high amount of portlandite from cement hydration. For larger particles, radiating cracks were found with formation of expansive gel inside the particles.
			2	[14],[19], [35], [38], [39], [47], [49], [36]

Line number	Parameter	Question	Influ-ence	Reference number
15	Fast reactive; mineralogy	*Does the composition of fast reactive aggregates influence the formation of gel?* - [38] found that the amount of soluble silica was similar for different particle sizes of an aggregate that showed different expansion. - There is a strong correlation between the expansion and the degree of reaction [4]. - Texture is more important than mineralogy. - The evaporated water is higher with reactive aggregates than for non-reactive. This water should come from the alkali-silica gel which gives an idea about the amount of gel produced. - Expansion does not necessary increase proportionally to the reaction degree or the amount of gel produced.	1	[4], [38] [14], [36], [48]
16	Pessimum? grading/ size distribution	*Do the size and/or the grading of pessimum content reactive aggregates influence the formation of gel? What about the quantity of gel formed?* - Smaller fractions react faster, but after prolonged exposure, expansions are of the same order for all fractions. - Larger sizes are slower and more gradual. - For each size fraction, maximum expansion occurs for pessimum content of the aggregate.	1	[13], [22], [47]
17	Pessimum? mineralogy	*Does the composition of pessimum content reactive aggregates influence the formation of gel?* - More reactive aggregates show maximum expansion at lower contents. - Higher opal contents lead to high amounts of gel that impregnate the cement paste and form a barrier to further penetration of NaOH, therefore causing a reduced expansion. - The mechanism at 1M NaOH, 80ºC is different from that in ASTM C227 which is related to Na_2O/SiO_2 ratio. - The expansivity of the gel seems to increase for higher ratio calcium/sodium, but this is controversial. - [44] tested opal by mortar bar tests and concluded that the larger expansion corresponds to the pessimum content of the aggregate. For higher contents, large amounts of gel are produced. Gel impregnates the cement avoiding further penetration of NaOH from the exterior solution.	1	[3], [28], [44]
18	NR-reference/ non-reactive?	*Does gel develop with non-reactive aggregates?* - Non-reactive aggregates can affect the expansion by contributing with additional alkalis. - It has been reported that non-reactive natural sands from different origins induced large variations in test results. - Limestone can contribute with calcium to the gel. - Also alkali-carbonate reactive aggregates have been reported to generate much lower expansion when test by AMBT. **Issue to be resolved.**	1	[3], [19], [26]

Line number	Parameter	Question	Influ-ence	Reference number
19	Water absorption	*Do the porosity and permeability characteristics of aggregates influence the formation of gel?* *What about the quantity of gel formed?* - Aggregates with higher porosity show higher degree of reaction, but the pores also store the reaction gel. - Manufactured sands have higher absorption capacity. - Tests using smaller grains of aggregate are more sensitive to denser aggregates such as tuffs and gneisses [61]. - Large particles of porous aggregates seem to cause larger expansion than smaller porous aggregates. - AMBT seems to be sensitive to more porous aggregates, but not suitable to evaluate reactivity of sands with many quartz crystals. - The porosity and permeability of the aggregate particles can influence the characteristics of gel considering that its composition is related to the location inside the concrete (inside aggregate particles or close to cement paste). - Microstructural and textural characteristics of the rock type play an important role in AAR and expansion processes (e.g. grain boundaries in microcrystalline quartz of mylonite).	1	[3], [4], [26], [61] [14], [31], [36], [46]
20	Filler type	*Does the presence/composition of filler influence the formation of gel?* *What about the quantity of gel formed?* - Calcareous filler allows denser packing of the cement paste and reduces the wall effect between aggregate and cement paste. - From products that can be added to clinker, filler is the less effective in controlling expansion. - [9] found that the addition of lime increases the expansion of the concrete, but concrete with non-reactive aggregate did not expand regardless of the presence of lime. - [48] says that the addition of filler reduces the unit concentration of the reactive aggregate resulting in less expansion. The reaction is less severe with inert filler added. - [50] refers that AMBT predicts effect of reactive rock fillers to inhibit expansion due to ASR, in contradiction to CPT, but the test of non-reactive limestone filler gave no effect. Conclusion: methods using very high temperature (e.g. AMBT) should not be used to evaluate the fillers containing silica. - CPT (40ºC) tests with GGBFS and FA show lower expansion [52]. - Lab tests using SCM avoid deleterious ASR when compared with field performance, probably because at high T and RH viscosity of gel decreases. Also, with slow reactive aggregates, SF reacts quicker and can inhibit ASR for higher temperature, but needs dilution of the pore solution. With fast reactive aggregates, ASR starts parallel to the pozzolanic reaction and prisms show no significant expansion during lab tests. [53] - The use of FA resulted in reduction of expansion for all aggregates. With SF expansion increases with increasing time and increasing alkalis in the mixture [54]. - The use of FA, slag and Li suppress the ASR expansion both in lab tests and in field conditions for some aggregates (e.g Spratt), but not all (e.g. Pittsburg) [60]. - The evaporation of water from samples is related with the pore structure of the mortar, which is affected by the presence of filler. - Existence of Ca appears to be essential for concrete expansion due to ASR (controversial) and for the formation of gel. Ca greatly increases the rate of reactive silica dissolution by maintaining a low solution silica concentrat.	1	[5], [9], [38], [25], [48], [50], [52], [53], [54], [60]

AAR References

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Influence of aggregate type on DEF during the exposure

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DEF				
Line number	**Parameter**	**Question**	**Influence**	**Reference number**
12	Slowly reactive; grading/size distribution	*Is there any relation between the occurrence of DEF and the grading/size of slowly reactive aggregates?* - There is an inverse correlation between aggregate particles size and expansion due to DEF. - Coarse aggregates may not have a significant role on the expansion in field concretes.	1	[2], [4]
13	Slowly reactive; mineralogy	*Is there any relation between the occurrence of DEF and the composition of slowly reactive aggregates?* - Contradictory conclusions: - Slowly reactive aggregates such as granite show expansion similar to fast reactive aggregates such as basalt [4]. - Granite shows higher rate of expansion than limestone and flint [15]. - Characteristics of ettringite are variable with different aggregates.	1	[3], [4], [15]
14	Fast reactive; grading/size distribution	*Is there any relation between the occurrence of DEF and the grading/size of fast reactive aggregates?* - Contradictory conclusions: - Width of cracks around aggregate particles is proportional to the size of the grains [5], [12] - There is no correlation between the width of cracks and the size of aggregates [2], [12]. - Some refer the homogeneous expansion of cement paste, which is independent from the composition of the aggregates. But there are some authors who refer that cracks are not resultant from the expansion of cement paste. Ettringite may form inside cracks originated by other processes.	1	[2], [4], [5], [12], [13]
15	Fast reactive; mineralogy	*Is there any relation between the occurrence of DEF and the composition of fast reactive aggregates?* - There might be a correlation, considering that DEF can be associated with AAR.	1	[2], [7], [13]

Line number	Parameter	Question	Influence	Reference number
16	Pessimum? grading/size distribution	*Is there any relation between the occurrence of DEF and the grading/size of reactive aggregates presenting a pessimum content?* - DEF is very difficult to reproduce in laboratory and there are just a few field confirmed cases of DEF. Also, it is difficult to prove that a field concrete was submitted to high temperature. - Contradictory conclusions related to pessimum: - Width of cracks around aggregate particles is proportional to the size of the grains [5], [12] - There is no correlation between the width of cracks and the size of aggregates [2]. - Some refer the homogeneous expansion of cement paste [14]. [2] has an opposite opinion due to discontinuous features of cracks around aggregate particles and variation of width around a particle.	1	[2], [4], [5], [12], [13], [14]
17	Pessimum? mineralogy	*Is there any relation between the occurrence of DEF and the composition of reactive aggregates presenting a pessimum content?* - There might be a correlation, considering that DEF can be associated with AAR.	1	[2], [7], [13]
18	NR-reference/ non-reactive?	*Is there any relation between the occurrence of DEF and the presence of non-reactive aggregates?* - Non-reactive aggregates such as limestone delay the DEF and reduce the expansion in mortars and concrete. - Limestone, due to dissolution at the surface, has an increased linking with the cement paste.	1	[3], [15]
19	Water absortion	*Do the porosity and permeability characteristics of aggregates influence the occurrence of DEF?* *What about the extent of DEF?* - Moisture is essential for the occurrence of DEF. If there is DEF associated with AAR, porosity might be important.	1	[13]
20	Filler type	*Does the presence/composition of filler influence the occurrence of DEF?* *What about the extent of DEF?* - Calcareous filler allows denser packing of the cement paste and reduces the wall effect between aggregate and cement paste. - The composition of filler can be important to the formation of thaumasite but direct references to DEF or ettringite were not found.	1	[5], [9]

References: See appendix 6.3.2

Influence of aggregate type on ettringite formed during the exposure

Author: Isabel Fernandes, University of Porto

Ettringite

Line number	**Parameter**	**Question**	**Influence**	**Reference number**
12	Slowly reactive; grading/size distribution	*Is there any relation between the formation of ettringite and the grading/size of slowly reactive aggregates?* - Large coarse aggregates can restrain the effect of the expansion due to the formation of ettringite. - Cracks filled with ettringite are more common around coarse aggregates than fine aggregates with the same composition.	1	[4], [10], [12], [15]
13	Slowly reactive mineralogy	*Is there any relation between the formation of ettringite and the composition of slowly reactive aggregates?* - The composition of fine aggregates has a marked effect on the amount of ettringite formed. - Slowly reactive aggregates such as granite show expansion similar to fast reactive aggregates such as basalt [4]. Concrete with granitic aggregates shows cracks around particles and extending to cement paste. - The mineralogy of aggregates (limestone) influences the microstructure of the interface aggregate-cement paste. - Characteristics of ettringite are variable with different aggregates. - Ettringite from internal origin may result from the existence of excess gypsum in cement or aggregates or the presence of sulfides, not directly related to slow or fast reactivity of aggregates.	1	[3], [4], [15]
14	Fast reactive; grading/size distribution	*Is there any relation between the formation of ettringite and the grading/size of fast reactive aggregates?* - There is an inverse correlation between aggregate particles and expansion due to sulphate attack. - The rate of expansion increases rapidly as the mean particle size decreases below 1 mm [4].	1	[1], [4], [12]

Line number	**Parameter**	**Question**	**Influence**	**Reference number**
15	Fast reactive; mineralogy	*Is there any relation between the formation of ettringite and the composition of fast reactive aggregates?* - More ettringite is formed in mortar bars showing higher rate of expansion. - Different fast reactive aggregates show similar expansion. - There might be a correlation, considering that the formation of ettringite can be associated with AAR. - [4] tested 6 aggregates (basalt, dolostone, granite, limestone, siliceous limestone and crystalline quartz). Only mortar bars made with quartz showed significant expansion.	1	[1], [2], [4], [7], [13]
16	Pessimum? grading/size distribution	*Is there any relation between the formation of ettringite and the grading/size of reactive aggregates presenting a pessimum content?* - There is an inverse correlation between aggregate particles and expansion.	1	[1]
17	Pessimum? mineralogy	*Is there any relation between the formation of ettringite and the composition of reactive aggregates presenting a pessimum content?* - There might be a correlation, considering that the formation of ettringite can be associated with AAR.	1	[2], [7], [13]
18	NR-reference/ non-reactive?	*Is there any relation between the formation of ettringite and the presence of non-reactive aggregates presenting?* - Non-reactive aggregates can contain minerals that release sulphate ion to the solution resulting in the formation of ettringite.	1	[1], [13], [15]
19	Water absortion	*Do the porosity and permeability characteristics of aggregates influence the formation of ettringite?* *What about the quantity of ettringite?* - The formation of ettringite in the gaps around aggregate particles depends on the aggregate quality. In concrete with mixed aggregates of different composition, ettringite forms preferentially around one of the types of aggregates. - Ettringite due to external sulphate attack is related to the permeability of the concrete, but ettringite forms easier when concrete is cracked by other processes (e.g. AAR). - Sulphate attack is difficult to reproduce in laboratory because field concrete is exposed to environmental conditions and sulphate from the exterior can be continuous available. In laboratory, sulphate in the immersion solution decreases with time and the pH increases.	1	[6], [13], [15]

Line number	Parameter	Question	Influence	Reference number
20	Filler type	*Does the presence/composition of filler influence the formation of ettringite?* *What about the quantity of ettringite?* - Calcareous filler allows denser packing of the cement paste and reduces the wall effect between aggregate and cement paste. - The presence of filler decreases the concentration of alkalis in the cement paste. Alkalis in the system increase the solubility of ettringite. - The composition of filler can be important to the formation of thaumasite and ettringite as the presence of calcium contributes to the formation of both minerals.	1	[5], [9], [13]

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RILEM – PERFORMANCE TESTING

Parameters influencing the lab/field correlation

A number of parameters was analysed concerning their influence on:

- Reaction products formed:
  - ASR gel
  - DEF
  - Ettringite
- Aggregate reactivity;
- ASR gel properties.

Parameters included storage conditions and aggregate type. For the majority of the parameters lots of references can be found to base a conclusion on their influence in what concerns the laboratory tests performance. However, there are also a number of questions not answered and limitations of the laboratory tests for which there is not yet a solution or the results obtained by different authors are not consensual.

There are some parameters for which no information was found. They are:

- Temperature of curing
- Temperature of measuring

It seems that these factors have a very low influence in the lab/field correlation or that they were not considered yet in the test parameters.

The comparison between results in the literature is not simple due to the fact that different laboratories use different standards. Also, for the same test, more than one variable is changed at the same time which complicates the attempt to find out which was the parameter influencing the result.

From the "desk research" developed it is concluded that none of the tests answer to the questions that arise from the table supposed to fulfil.

Some points will be discussed before going through the different columns and lines of the table.

AAR

Storage conditions

The main issues in the possible laboratory/field correlation regarding storage conditions seem to be:

- Humidity
- Temperature
- Alkalis in the environment

In fact, the humidity simulates a great number of situations in real structures, but it works in a very different way when combined with temperature. The conditions therefore created do not reproduce the exterior exposition of concrete (unless it is a swimming pool or a construction on thermal environment).

Humidity shows a higher importance on expansion in humid environment compared with submerged samples. Temperatures will be much lower in structures, unless very special situations are considered (structures exposed to thermal hot waters). The amount of water available is important if both silica and alkalis are present, otherwise it will not (obviously) contribute to the reaction. Humidity, however, has an influence in the viscosity of gel, thus affecting the expansion. Humidity is also tested in the laboratory with wrapping or not the specimen. This process has a direct influence on the leaching of alkalis and leaching is much strong for smaller specimens.

This fact leads to another question: one of the problems in laboratory tests is the leaching of alkalis, but tests are performed with an increased amount of alkalis. In this context, aren't the results just the answer to a wrong formulation? What would happen with an amount of alkalis consistent with the attempt to avoid AAR (limited alkalis according to standards for concrete production)?

Temperature accelerates the reaction, meaning it will start earlier and at a higher rate, but it does not influence the "amount" of reaction (which is just dependent on the availability of the components). Therefore, temperature in any case is too severe in comparison with field exposure. It is convenient in that it shortens time of the tests (which is critical for construction industry) and in this context it is acceptable that tests are run on high temperatures.

Regarding external alkalis, the development of the reaction is dependent on the composition of the solution (chemical compound used). However, is it reasonable to consider at the same time external alkalis and high temperature? This seems to correspond to very specific situations: in field exposure, external alkalis mainly come from salts used for de-icing, meaning they are applied with very low temperatures. It may be important just if limit conditions are to be known (with a very probability of happening).

Aggregates

Regarding the characteristics of aggregates, it is recognized that the type of rock has a great influence on the rate and extent of reaction (more reactants available mean more reaction). The type of rock is related to its "composition" (shouldn't it be called microstructure as the main component is always some sort of silica?).

Regarding the size of aggregate particles, it has been noticed that for smaller particles there is lower expansion. This fact is attributed to the destruction of microstructure of the rock when crushed to small sizes. This may be the cause for the bad results of AMBT in the evaluation of slowly reactive aggregates.

Porosity of aggregates, also related to the type of aggregate, allows the fluids to contact a large surface of reactive silica and therefore enhances the reactivity. But the pores also store the gel, decreasing the expansion of specimens. In what extent each of the two-fold aspects contributes is not yet clarified.

The definition of "innocuous" aggregate is also to be discussed: there are reports of expansion in tests performed with innocuous aggregate.

Composition of the gel

The composition of the gel is dependent on the location within the concrete and probably with the composition of the aggregates (cannot confirm this logical statement, my experience tell me the opposite!). It also depends on the type of alkalis available (external alkalis).

According to literature, the composition has an influence on the expansivity of the specimens (Calcium present or not). There is a direct connection between the expansion and the viscosity of gel, which is enhanced by the amount of water, leading us again to the storage conditions (humidity).

There is not a lot of information about "inert" fillers (e.g. lime), but it seems not to be effective in controlling expansion. Other cement substitutes (e.g. slag, fly ash, silica fume) are much more effective in avoiding/delaying the AAR.

DEF/Ettringite

DEF is difficult to reproduce in laboratory and, in consequence, a correlation is almost an "utopia".

The possible correlation between DEF/ettringite and the aggregate type can only be raised if it is assumed that the reaction is associated with AAR. Even though, some experiments with different types of aggregates gave similar results regarding expansion.

The same applies to the size of aggregate: is it well established which is the mechanism causing expansion when DEF occurs? Is there an homogeneous expansion of the cement paste (independent from the type of aggregate) or can it be accepted that there is a correlation between the size of aggregate particles and the cracking/expansion?

Porosity of aggregates can enhance the formation of ettringite in that more porosity represents more available water in the system.

AAR

1. THE INFLUENCE OF STORAGE CONDITIONS ON AGGREGATE REACTIVITY (see Appendix 5)

Some parameters of storage conditions seem to be of the highest interest concerning the occurrence of ASR and the amount of product formed, factors that condition the expansion in mortars and concretes. From these parameters, temperature of exposure, the existence of humidity and alkalis in the system should be highlighted. There is a rich literature about these parameters and about other parameters with influence in the process of ASR.

There are also some parameters for which just a short number of references was found or not found at all:

- Temperature of curing of specimens (mortar of concrete), which is referred not to be relevant for the occurrence of ASR;
- Temperature of measuring of specimens, which depends on the type of test performed. As a laboratory good practice, the temperature should be maintained for a given set of tests.

1.1 Is there an influence of the temperature of exposure on the reactivity of aggregates?

Experiments show that there is an influence of temperature on aggregate reactivity. However, this parameter should not be analysed isolated, as it works simultaneously with other factors.

In general, high temperature can induce higher rate of reaction, a greater amount of gel is formed and higher expansion is observed. From the chemical point of view, however, this is not correct as temperature can act as a “facilitator”, but the amount of reaction is exclusively related to the amount of reactants available. Also temperature seems to activate “non-reactive” aggregates.

Some laboratory tests show results different from those, with lower expansion at higher temperature for the similar specimens. Authors explain this phenomenon referring to the occurrence of drying of specimens, alkali leaching and changes in the pore solution composition. Leaching of alkalis is an important factor to consider as it contributes to the decreasing of pH of pore solution with decrease of solubility of quartz. Leaching is higher for the CPT60ºC than for the CPT38ºC, meaning that for the long term the expansion will be higher for the lower temperature. For field conditions, higher temperatures produce faster expansion.

1.2 How does the duration of tests affect the aggregate reactivity?

For reactive aggregates, lab tests show that expansion increases on increasing the duration of the test. The behaviour is different when comparing sedimentary aggregates with igneous and metamorphic rocks, meaning that the aggregates react in a different way. Time has no effect for non-reactive aggregates. With time, a larger amount of ASR gel is produced, leading to a higher expansion. The amount of gel is dependent on the available silica and alkalis. In this context, the highly reactive aggregates will have more silica for reaction and more gel will be produced with time, as long as there are alkalis and water in the system.

1.3 Does the size of specimens used in tests influence the results obtained?

Many references are found concerning the expansion of the prisms, but seldom related to the aggregate reactivity.

Large prisms expand slower at start, but they continue to expand at a steady rate. When testing extremely reactive aggregates, smaller specimens expand more. This fact leads to the conclusion that there is an influence of prism size on expansion and that this expansion is related to the aggregate reactivity. Tests performed in order to explain this influence, lead to the conclusion that the larger the cross-section of a concrete prism, the greater the expansion, which is interpreted as being caused by more pronounced alkali leaching effect of smaller specimens.

1.4 Does the presence of humidity and alkalis in the concrete or mortar mix influence the reactivity of aggregates?

These are important factors and they both are necessary for the reaction to take place. The presence of water and alkalis does not influence the reactivity of aggregates, but the extent of the reaction. Therefore, for a specific aggregate, more alkalis available mean more expansion.

There are a large number of papers concerning the quantity of alkalis added to the mortar or concrete mix. For a specific test, it is verified that the result for the same aggregate may run from "innocuous" to "reactive" depending on the content of alkalis available for reaction. The percentage of alkalis used in lab tests is higher than the one applied in field concretes, as standards regarding the avoidance of ASR state a limit to the weight percentage of alkalis. In this respect, some of the tests are much more severe than field conditions, meaning the evaluation of reactivity is performed on the "safe" side, or for the worst conditions admitted. In lab tests it is verified that alkali content decreases in pore solution due to leaching in high moisture environment and also that leaching occurs specially in small specimens. Pore solutions in field concrete are mostly not subject to alkali leaching, and therefore the variation of alkalis in concrete should stay constant.

Origin of alkalis from other sources such as aggregates and admixtures should be considered, as specimens exposed outdoor with low alkali content show ASR.

Concerning the quantity of water in the system, it is known that water facilitates exchanges and promotes reactions, in the same way for reactive or non-reactive aggregates. Therefore, there is an influence of the presence of water in the mix.

1.5 What is the influence of type of container, the water level and the submersion of specimens on alkali reactivity?

Although these parameters were set in different lines of the draft table, they should be studied together as they interfere with each other. Most of the experiments performed deal with:

- Type of container;
- Wrapping (or not);
- Above water or submerged.

One of the premises for ASR to happen is that enough water should be available for reaction. No direct reference was found connecting the external humidity to the reactivity of aggregates as it seems to influence in a higher degree the rate of reaction and the amount of products formed, resulting in increased expansion.

It has been observed that the quantity of gel produced is far inferior when there is no external water supply and also that the higher humidity leads to higher expansion. However, after completion of the reactions (depending on silica and alkalis available), any added water will not cause extra expansion. However, if there is still silica and alkalis available for reaction and a lack of water occurs, expansion will stop. It will be quickly reactivated if water is again in the system.

Mortar bars and concrete prisms tested in lab show higher expansion when stored in sealed containers above water compared to unwrapped bars stored above water, while bars and prisms stored in a moist room show the least expansion and the greatest extent of alkali leaching. Alkali leaching seems to be more severe for small specimens. The problem of alkali leaching is a big challenge in lab expansivity tests.

Due to contradictory results in different papers, the research **was inconclusive** in what concerns the type of container (thought it seems not to be of a great importance) and the use of wrapping, which leads us to the next question: alkalis.

1.6 What is the influence of external alkalis in the lab tests of aggregate reactivity?

When alkalis are added to the immersion solution, the influence of the cement alkali content on mortar bar expansion significantly decreases.

It has been verified that different aggregates react in a different way when exposed to salt solutions and also that the reaction is dependent of the salt used (NaOH, NaCl, KOH, LiOH or just R.H.).

The dissolution of silica varies with the compound in the solution, but the amount of dissolved silica tends to be independent from the composition of alkalis over time.

Although there is no direct reference to the influence on aggregate reactivity, the fact that the solubility of silica is dependent of the compound means that there is an influence of this parameter.

2. THE INFLUENCE OF STORAGE CONDITIONS ON PROPERTIES OF ASR-GEL (see Appendix 6.1B)

Most of the papers about storage conditions link the reactivity of aggregates and the expansion of specimens, which is easy to understand knowing that the amount of gel produced is dependent on the aggregate reactivity (available silica) and higher amount induces higher expansion. As a matter of fact, it is sometimes difficult to separate both subjects.

There are some works that highlight the expansion as a function of the composition of gel, which is related also to a number of factors of storage conditions.

2.1 Is there an influence of temperature of exposure on the rate or formation of ASR products or on their properties?

There are a great number of experiments performed with varied temperature for similar specimens, but with other variable test conditions simultaneously. It is observed that higher temperature results in a greater amount of Ca in the composition of the gel, assumed by some as a prerequisite for the formation of expansive gel. Viscosity of the gel decreases with increasing temperature, meaning the expansion will be lower.

Regarding other properties of ASR gel, it was found that products obtained in lab tests are similar to those identified in field concretes (amorphous and crystalline). This fact is important as it means that temperature is probably not as important to the properties as it is for the reactivity, rate and amount of gel produced.

2.2 How does the duration of tests affect the properties of gel?

With time, a larger amount of ASR gel is produced, leading to a higher expansion. There is no direct indication to the correlation between time and the properties of gel. However, it is known that the composition of gel evolutes with time: at start gel absorbs lots of water, but does no exert significant pressure, while in later stages, due to the evolution of the reactions, Ca content increases and gel becomes more viscous and expansive than the alkalis-rich gel.

2.3 Does the size of specimens used in tests influence the properties of gel?

There are references to the increase in expansion with the increase in prisms cross-section. This variation in expansion seems, however, to be connected to the composition of the aggregates and to the amount of alkali leaching (higher for smaller specimens) and not exactly to the properties of gel. In smaller specimens, exudation of gel should be easier than in larger prisms. In real structures, exudations are composed by alkali-silica gel with no Ca. This issue should be investigated in order to compare the composition of gel inside smaller and larger prisms with field concrete (large cross-section) by using petrographic methods.

2.4 Does the presence of humidity and alkalis in the concrete or mortar mix influence the properties of gel?

Alkalis and water are essential for ASR to occur. In a study about expansive pressure originated by gel, it was found that the amount of alkalis and water is proportional to the amount of gel formed. However, mortars containing ASR gel with higher alkali content than a critical value show extremely low expansive pressure.

Alkali gel is considered non expansive compared to gel containing Ca, which is a function of the place where gel occurs inside the concrete and also of the age of the gel.

Stress induced in concretes depends on the composition and amount of gel produced.

2.5 What is the influence of type of container, the water level and the submersion of specimens on the properties of ASR gel?

As stated before, this analysis will include the three factors that seem to be connected:

- Type of container;
- Wrapping (or not);
- Above water or submerged.

It has been observed that the quantity of gel produced is far inferior when there is no external water supply and that dry specimens originated no products. For specimens stored in high humidity, it was observed that when immersed, they absorb a large quantity of water. Immersion lowers expansion due to alkali leaching.

The question on container/wrapping and water level seems to influence more the amount of gel than the properties of gel. Expansion is usually in literature connected to the amount of gel and not to the composition, when referring to storage conditions. However, it should be clarified in what extent the existence of alkali leaching can influence the composition of gel, regarding the content of Ca and alkalis.

2.6 What is the influence of external alkalis in the lab tests?

Test specimens with different salts dissolved in container water lead to the conclusion that the products formed differ in composition. NaOH is the more aggressive and produces a greater amount of gel. KOH produces more crystalline gel. It has been observed that there is little difference in composition of the gel formed in mortars immersed in NaOH with and without calcium.

The dissolution of silica varies with the compound in the solution, but the amount of dissolved silica is independent from the composition of the alkalis over time.

Expansion increases for higher concentration of alkalis (not consensual) in the solution. Expansion is also dependent on the salt used in the immersion solution (e.g. NAOH, NaCl). These facts may influence the reactivity and amount of gel produced, but the effect on gel properties in not clear.

In literature, it is referred that the expansion increases until a certain level of alkalis is reached and then decreases for higher contents, concluding that there is a "pessimum" effect of external alkalis (probably related to available silica).

3 THE INFLUENCE OF AGGREGATE TYPE ON ASR-GEL

(see Appendix 6.2)

3.1 Influence of size and grading of aggregates

The influence of grading and size on the formation of ASR gel depends on the nature, texture and composition of the aggregate. There are different opinions dependent on the aggregate being slowly reactive, fast reactive or showing pessimum content.

For slowly reactive aggregates such as granite, the use of very fine aggregates can destroy the original microstructure characteristic of the rocks, underestimating the alkali reactivity of the rocks in the accelerated tests (e.g. size used in AMBT and Chinese autoclave method). These tests fail to identify the reactivity of some slowly reactive aggregates (based on field performance).

For fast reactive aggregates, opinions are contradictory:

- The larger the size of the aggregate particles, the higher the expansion (e.g. in AMBT) (e.g. siliceous limestone); larger particles lead to smaller expansion at early ages, but increase continuously at later ages.
- Larger expansion occurs for medium sized or low sized particles.

Smaller fractions react faster, but after prolonged exposure, expansions are of the same order for all fractions. Larger sizes are slower and more gradual. For each size fraction, maximum expansion occurs for pessimum content of the aggregate.

The shape of the particles is also important. It was verified in lab that the effect of size on ASR is more pronounced in crushed aggregates than in natural sands (not consensual).

Although classified as alkali-silica non-reactive, alkali-carbonate reactive rocks should be considered, as they can influence results when they also present ASR.

In tests and field concrete, it is observed by petrography that fine particles show different behaviour from coarse aggregates. It is usual to find larger particles with cracks extending to the cement paste and partial substitution by gel in rims and along the interstices between quartz grains. In small particles, gel usually substitutes at a higher rate the silica in the grain, but without visible expansion. These features can be concomitant, showing the direct influence of size in the reactivity of aggregates.

The influence of grading and size on gel properties seems to be related to the presence of calcium. Ca-rich ASR gel was identified around fine quartz particles due to high amount of portlandite. In cracks, Ca rich gel is found at larger distance from the coarse aggregates due to exchanges with the cement paste, but usually it is not detected inside reactive particles.

Issue to be resolved: the importance of the shape/origin of aggregates (natural, manufactured, crushed).

3.2 Is there a difference on ASR related to the mineralogy of aggregates?

The analysis of reactivity of aggregate is dependent on the mineralogy, but also on the texture of the aggregate. There are reports from field concrete confirming the occurrence of ASR and gel formation in concrete with slowly reactive aggregates.

For fast reactive aggregates, it was found that the amount of soluble silica was similar for different particles sizes of a certain aggregate, but the expansion varied for different size fractions.

Concerning the aggregates with pessimum content, more reactive aggregates show maximum expansion for lower contents of reactive silica.

Studies developed with non-reactive aggregates show that some sands from different origins induced ASR.

It should also be considered the possible contribution of aggregates to alkalis in the system and of limestone with calcium to form the gel.

Mineralogy and texture are the main characteristics in an aggregate influencing the occurrence of ASR and the amount of gel produced. Petrography should be always used.

Analyses of gel by EDS in field concrete with aggregates of variable composition (granites and limestones) show no significant difference in the composition of gel. It has been verified that expansion does not necessarily increase proportionally to the reaction degree or the amount of gel produced. It seems to be dependent of Ca content, which is variable according to location inside the concrete.

For aggregates showing pessimum content, it was referred that the larger expansion of specimens corresponds to the pessimum content of the aggregate.

For non-reactive aggregates, expansion is slower than with reactive aggregates, but this must be a consequence of the rate of reactivity and not of the properties of gel.

3.3 Does water absorption influence the development of ASR products?

There are just a few references to this parameter in literature. Aggregates with higher porosity show higher degree of reaction (e.g. sandstone, quartz with sub-granulation), because they are more easily penetrated by pore solution and have a higher specific area exposed to the solution. These pores and interstices also store gel, influencing the expansion that could result from its formation. Water absorption decreases the viscosity, but increases the amount of gel.

The porosity of aggregates influences the properties of gel considering that its composition depends on the location inside the concrete. Micro-structural and textural features of aggregates play an important role in expansion processes. Grain boundaries and the presence of microcrystalline quartz (e.g. in mylonite) will produce higher amount of gel.

However, concerning the water absorption of gel, the volume should increase, but the direct connection to higher expansive pressure is not clear.

3.4 Does the addition of calcareous filler contribute/prevent the occurrence of ASR?

Difficult to answer, as information was not found in the literature. Calcareous filler reduces the expansion caused by ASR, due to the reduction of unit concentration of the reactive aggregates, but it is the less effective of the products that can be added to concrete.

The presence of filler influences the pore structure of mortar and, consequently, the evaporation of water, which can affect the chemical exchanges and the rate of reaction.

The existence of Ca appears to be essential for concrete expansion due to ASR (controversial). Ca greatly increases the rate of reactive silica dissolution by maintaining a low solution silica concentration.

4 DELAYED ETTRINGITE FORMATION (DEF) (see Appendix 6.3.1)

The hypothesis formulated about products formation concerned the aggregate type. DEF is thought to result from high temperature during the cure of concrete, either due to steam-curing or to the existence of wide volume of concrete. It is a phenomenon difficult to reproduce in laboratory, mainly in what concerns the production of large volumes of concrete. It seems not to be easy to prove that a certain field concrete was submitted to high temperatures, therefore compromising the confirmation of DEF field cases.

4.1 Influence of size and grading of aggregates

In the literature, two contradictory opinions are found. Some authors refer that the cracks found around aggregate particles, typical of DEF, are not caused by the growth of ettringite crystals, but to the homogeneous expansion of the cement paste. Ettringite just infill the open spaces in the interfaces, being mechanically passive.

Other scientists state that the width of cracks is proportional to the size of the particles. However, field concrete supposed to have had DEF shows cracks that are discontinuous around the particles and also have variable width around the same particle. Most of the cracks also extend to the cement paste. It is also verified that cracks occur more frequently around coarse than sand particles with the same composition. All these facts oppose to the theory of homogeneous expansion.

There is also an additional factor to be considered which is the possible association between DEF and ASR. Some authors refer to ASR as the cause of cracking, being the cracks filled by ettringite.

4.2 Is there a difference concerning the mineralogy and reactivity of the aggregates?

There are references to DEF in concrete with different types of aggregate, from slowly reactive to aggregates that present a pessimum content. There might be a correlation between the type of aggregate and the rate of reaction, considering the possible association with ASR.

Concerning non-reactive aggregates, limestone is known to delay DEF and reduce the expansion in mortars and concretes in lab tests, which might result from the increased linking between limestone and the cement paste.

The presence of sulphides in the aggregate should also be considered, as it might contribute to the formation of ettringite in this type of sulphate attack.
Issue to be resolved.

4.3 Does water absorption influence the development of DEF?

It was assumed that the water absorption refers to the porosity and permeability of the aggregate.

Features characteristic of DEF do not include the presence of ettringite inside aggregate particles, except in grains of the sand fraction containing sulphides.

Although references from literature are scarce, it seems that there should be a very marginal influence, except if DEF is associated to ASR.

4.4 Does the addition of calcareous filler contribute/prevent the occurrence of DEF?

Difficult to answer, as there was not found information in the literature. Filler allows denser packing of the cement paste and reduces the wall effect between the aggregate particles and the cement paste, which might prevent the occurrence of cracks in the interfaces. Calcareous filler is known to influence the formation of thaumasite from TSA. The importance to DEF should also be studied.

5 ETTRINGITE FORMATION (see Appendix 6.3.2)

Ettringite is formed as a primary product during the curing of concrete. Deleterious ettringite results from:

- TSA – Thaumasite Sulfate Attack
- ISA – Internal Sulfate Attack
- DEF – Delayed Ettringite Formation
- External sulfate attack.

There is a very rich literature about TSA and DEF and a little less about ISA and external sulphate attack. The questions to be answered were mainly related to the size of aggregate particles and to their reactivity.

5.1 Do the size and grading of aggregates influence the formation of ettringite?

For authors who believe that expansion is due to the formation of ettringite crystals, the presence of large aggregates restrains the effect of expansion.

Although the cracks with ettringite are more frequent around coarse particles, there is an inverse correlation between the size of the particles and the expansion due to ettringite formation.

5.2 Does the composition and reactivity of aggregates influence the formation of ettringite?

In field concrete, it has been observed that when there are particles of different compositions, ettringite is formed mainly close to one of the types of aggregates. However, generally the different composition is related to different sizes of particles and the two variables can be involved. It is then difficult to find out which factor prevails.

Just one reference was found about the correlation between expansion and the occurrence of siliceous aggregates.

The composition of aggregates may be important in case they contain sulphides, which can occur even for non-reactive aggregates.

Issue to be resolved by testing more aggregate types, maintaining all the other parameters constant. It is obvious that if ettringite formation is connected to ASR, more ettringite will be formed for fast reactive aggregates than for slowly or non-reactive aggregates. Considering that more expansion exists when more ettringite is formed, then more ettringite should exist for fast reactive aggregates showing pessimum effects, which is not really the case.

5.3 Is there a correlation between water absorption and the occurrence of ettringite?

Porosity of the concrete is important for ettringite formation due to an easier transport of the ions entering the reaction. However, in what concerns the porosity of aggregates, there is not a direct relation with ettringite formation unless it is originated by the presence of sulphides.

5.4 Is filler important to prevent the formation of ettringite?

The presence of filler might have an indirect role as it contributes to decrease the concentration of alkalis and this increases the solubility of primary ettringite.

From the analysis carried out, it is concluded that questions concerning the role of the size and composition of aggregates are not yet clarified. However, other parameters might be more important such as the storage conditions. Also, TSA has not yet (I think!) been analysed by RILEM.

6 THE INFLUENCE OF AGGREGATE TYPE ON AGGREGATE REACTIVITY (see Appendix 5)

The aggregate reactivity is obviously dependent on the type of aggregate. The rate of reaction as well as the amount of products formed is a function of the aggregate type.

Tests performed show that grading has an influence on the reactivity. Features associated with ASR are different for fine and coarse particles of a specific aggregate. Some aggregates show higher expansion for larger particles, some for intermediate sized particles, and sometimes small particles have stronger reactivity. Different tests use different grading of particles, and when very small sizes are used, the structure of the rock may be destroyed leading to a false result.

The classification as slowly reactive, fast reactive and non-reactive should be based on field performance, which is not always possible. However it is known that, in special for slowly reactive aggregates, the accelerated expansivity tests may give false results of non-reactivity. The reverse may happen with non-reactive particles that are classified as reactive, because the conditions in tests are too severe for some types of aggregate.

The classification of non-reactivity is not universal. Tests performed with different non-reactive natural sands mixed with a specific reactive aggregate show different results and sometimes expansion was registered.

The composition of gel seems not to be dependent on the nature of aggregates. Gel with varied composition regarding the Ca content was identified in the same sample, with different composition from one grain to another and also in the same grain.

Calcareous filler seems to decrease the concentration of alkalis in pore solution, decreasing the reaction independently of the reactivity of the aggregate. Filler also contributes with Ca which is necessary for the formation of gel.

The challenge regarding the identification of reactivity of aggregates is, at the present moment, to find an accelerated test that can correctly classify aggregates, in special those considered non-reactive or slowly reactive. It would be recommended that all the aggregates were classified by petrography before performing tests. In particular for slowly reactive aggregates, petrography has demonstrated to be the method which gives results closer to field performance.

The influence of calcareous filler should be investigated further due to costs involved.

7. CONCLUSION

This review just confirms the well known fact that laboratory tests do not reproduce field conditions and that there is yet a long way to go in order to correctly evaluate the reactivity of aggregates by tests.

Field performance is better evaluated by blocks exposed outdoor, but this experiments are usually too long to be compatible with tide timetables of construction businesses.

Laboratory tests seem to give a good idea about the reactivity of fast reactive aggregates and also to identify the presence of a pessimum content, characteristic of some aggregates. However, the tests known at the present moment may fail to characterise slowly reactive aggregates and also the so-called non-reactive aggregates. For these groups in particular, petrographic assessment of aggregates should be mandatory.

There is a great number of papers published about lab tests that just refer (and not always) the nature of the aggregates. It is well known, and RILEM committees had been working on the subject, that the designation of a rock is far from the least needed to identify potential reactivity, most of the times related to microstructure and texture of the rock.

Petrography might also be useful in the study of samples after tests are performed in order to find out what is the real importance of particle size and composition in the development of gel and on expansion of specimens. Also for this parameter, contradictory results are obtained.

The factor leading to more or less expansivity of ASR gel is not completely clarified, as different opinions are found on the importance of calcium. Why do cracks inside large particles of aggregate show low Ca gel when they are the origin of the cracks that extend to the cement paste and also the origin of expansion? ***Issue to be resolved.***

Regarding sulfate attack, it would be interesting to understand the origin of cracks observed in DEF. More tests are needed, although the reproducibility of field conditions is not easy to be obtained in lab.

TSA is another subject that should have more work developed in what concerns lab tests. Most of the literature is about case studies but the preference of the formation of thaumasite instead of ettringite is not completely clear.

Procedure for sampling and measurement of alkali leaching during concrete prism testing

The following procedure has been developed and applied by Jan Lindgård as part of his PhD study. The principle is to sample water from the bottom of the CPT storage containers at given intervals and measure the content of alkalis present. At the end of the test, also the alkalis that may have been sucked up in any lining used should be measured.

Preparation of storage container

Before starting the test, make sure that the storage container, including the bottom grid, is clean. If needed, also apply a weak acid. After cleaning the container, wash with deionized water.

Always apply new lining (if applied). Only deionized water shall be used to wet the lining (if applied) and to fill the bottom of the storage container.

Avoid any contamination of the equipment used.

Measurement of volume water

At every sampling, the volume of the water in the bottom of the storage containers must be known. Due to sorption of water by the concrete prisms and by the lining (if applied), weighing of the containers will not be accurate. A more suitable procedure is to prepare a plot with volume water versus height of the water. After wetting the lining (if applied), fill up the container successively and measure the water depth in the centre of the container bottom. At SINTEF, a wooden pin is applied for measuring, see Fig. 1. If the bottom grid lies in the bottom at sampling of liquid, also place it in the bottom before preparing the height-volume plot.

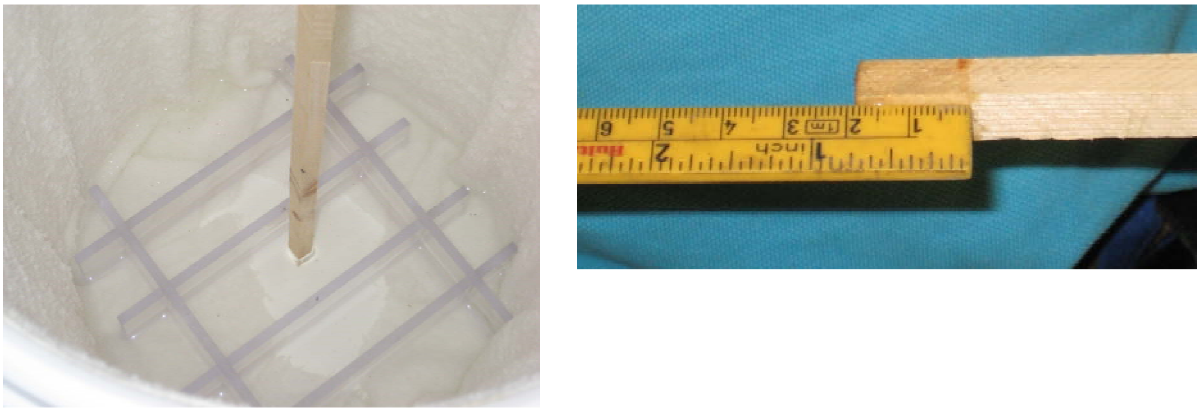

Figure 1. Measurement of height of the water in a container by use of a wooden pin.

Sampling of liquid

Make sure to measure the height of the water before each sampling as basis for calculating the volume of water. To homogenize the distribution of alkalis, stir the water before sampling. Apply a clean pipette (or similar) to suck up approx. 20 ml of water, see Fig. 2. Fill the sample on a clean plastic bottle able to resist alkalis without disintegrate or contaminate the sample with supplementary alkalis. If a bottle has been used before, clean it by applying a weak acid solution, before washing it with de-ionized water. Before taking the next sample, clean the pipette with deionzed water.

Figure 2. Sampling of water in a container by use of a pipette (left). Plastic bottle for storage of the water sample (right).

After sampling, add 20 ml deionized water to the container. Also add deionized water to compensate for any evaporation (i.e. add water up to the amount described in the test method).

Measurements, calculations and report
Measure the content of alkalis, [Na] and [K] (mg/l), in the 20 ml samples by use of flame atomic absorption spectroscopy (FAAS), inductively coupled plasma mass spectrometry (ICP-MS) or alternative equipment with comparable accuracy. Calculate the content of alkalis (mg/l) in the samples as [Na_2O], [K_2O] and [Na_2O_{eq}], respectively.

Calculate the volume of the water (l) in the storage container on the basis of the measured water heights. Calculate the cumulative amount of alkalis (g) leached out from the concrete prisms versus time. Account for the content of alkalis present in all previous 20 ml samples removed. Report the cumulative alkali leaching as reduction in the concrete alkali content, both expressed as *kg alkalis (i.e. Na_2O, K_2O and Na_2O_{eq}, separately) leached per m^3 concrete* and as % *alkalis (i.e. Na_2O, K_2O and Na_2O_{eq}, separately) leached* compared to the origin alkali content in the concrete at the time of mixing, see Fig. 3.

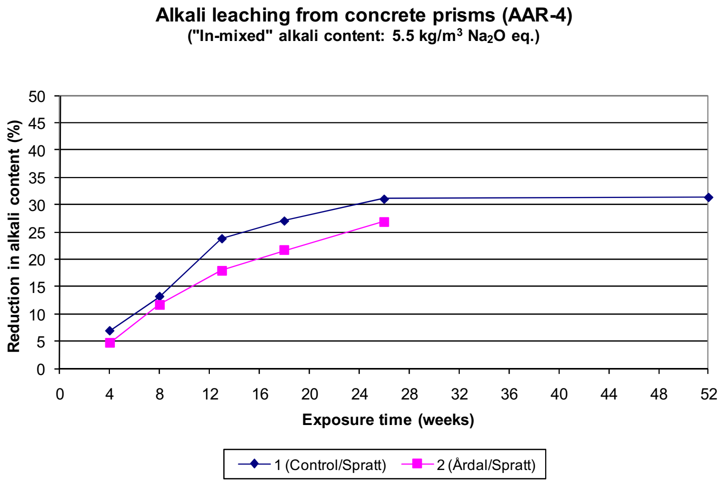

Figure 3. *Example of presenting results from measurement of alkali leaching (comment: no lining was applied, thus the last reading represents the total alkali leaching).*

Any alkalis present in the lining – total amount of alkalis leached

At the end of the test, also the alkalis present in the lining (if applied) should be measured. Either apply the whole lining, or divide the lining into representative samples. According to SINTEFs procedure, the lining is cut into three pieces; top, middle and bottom part, respectively. In this way, also the content of alkalis versus height above the water may be measured. The lowest part of the lining is slightly twisted inside the container to remove excess water.

After removing the lining, stir the water in the bottom of the container and sample 20 ml, before measuring the volume of the liquid by pouring the water into a separate container and weigh it (account for the 20 ml of water removed).

Submerge each lining sample in approximately 1.5-2 litres of deionized water (the exact volume of water must be measured) in a clean plastic container / plastic bottle able to resist alkalis without disintegrate or contaminate the sample with supplementary alkalis. If the container / bottle have been used before, clean it by applying a weak acid solution, before washing it with deionized water. Add a lid or screw cap to avoid evaporation. Stir or shake the liquid once a day for one week. After one week, stir once more, and sample 20 ml of the liquid by use of a similar procedure as applied for sampling from the containers (see above). Measure and calculate the amount of alkalis leached out (as described above).

Calculate the total amount of alkalis leached out during the exposure period as the sum of alkalis present in the lining samples and the alkalis remaining in the bottom water after removing the lining. Account for the content of alkalis present in all previous 20 ml samples removed.

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