



Durability performance assessment of non-standard cementitious materials for buildings: a general method applied to the French context

Pierre Pimienta, Blandine Albert, Bruno Huet, Michaël Dierkens, Philippe Fransisco, Patrick Rougeau

► To cite this version:

Pierre Pimienta, Blandine Albert, Bruno Huet, Michaël Dierkens, Philippe Fransisco, et al.. Durability performance assessment of non-standard cementitious materials for buildings: a general method applied to the French context. RILEM Technical Letters, 2016, 1, 10.21809/rilemtechlett.2016.17 . hal-03752764

HAL Id: hal-03752764

<https://cstb.hal.science/hal-03752764>

Submitted on 17 Aug 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Durability performance assessment of non-standard cementitious materials for buildings: a general method applied to the French context

Pierre Pimienta^a, Blandine Albert^b, Bruno Huet^{b*}, Michael Dierkens^c, Philippe Francisco^d,
Patrick Rougeau^d

^a Université Paris-Est, CSTB, 84 avenue Jean Jaurès Champs-sur-Marne, 77447 Marne-la-Vallée Cedex 2, France

^b LafargeHolcim R&D, 95 rue du Montmurier, 38291 Saint-Quentin-Fallavier Cedex, France

^c CEREMA, 25, avenue François Mitterrand - CS 92 803, 69674 Bron Cedex, France

^d CERIB, 1 Rue des Longs Reages, 28230 Épernon, France

Received: 30 September 2016 / Accepted: 05 December 2016 / Published online: 28 December 2016
© The Author(s) 2016. This article is published with open access.

Abstract

This letter focuses on the technical assessment of new products or systems in the Building sector before being placed on the market in the French and European context. In particular, it discusses the assessment of the durability aspect of innovative products or systems based on cementitious materials that do not meet specifications of standards. After a brief review of the regulatory context and existing assessment procedures, an example of method of assessment is proposed. There are six successive stages, from describing an invention to choosing relevant testing methods and assessment criteria. Thematic fact sheets describing the different kinds of known alteration for cementitious materials and associated performance assessment methods are presented. An applicant and an assessor are invited to expand the scope of their investigation in case of significant technological leap forward that involve the use of a product/system in a field of application that may not be covered by the current fact sheets.

Keywords: Assessment; Cementitious materials; Durability; Testing; Non-standard

1 Introduction

1.1 Innovation in the building sector

The building sector is dynamic and involves various actors who are constantly innovating to meet the challenges of their time and to anticipate those to come in the future. Since the large post-war construction projects until recently, these innovations were mostly focused on improving architectural quality, reducing cost, improving worker safety, etc. The new challenges for which the sector is mobilized are the climate change, the economy of natural resources, and user health and comfort. In these areas, recent advances have reduced the overall environmental impact of buildings (reduction of the carbon footprint of materials and of construction and renovation processes, improving building energy performance, installing alternative non-fossil fuel heating systems, etc.). User health and safety are a constant concern, such as volatile organic compound assessment.

Finally, the use of new technologies makes day-to-day life easier with more connected, more "intelligent" buildings.

Research and development has put in a lot of effort and the accelerating rate of innovation in many areas of construction is creating a large number of new building materials and systems. Furthermore, expectations are high and these innovations must be brought to market quickly.

In many cases, these new products and systems comply with the specifications of existing standards. However, when there is a large technological leap forward, standards, structural calculation methods, and current reference texts dealing with their implementation may not always cover the use of product or the system in the targeted field of application.

The drafting of new standards or the adaptation of existing ones to these new products is one possible way forward, but this often involves timelines that are not compatible with the need to place products on the market rapidly. Therefore, in order to speed the arrival of non-standardised products on

* Corresponding author: Bruno Huet, LafargeHolcim R&D, 95 rue du Montmurier, 38291 Saint-Quentin-Fallavier Cedex, France, bruno.m.huet@lafargeholcim.com

the market, industrial players may appeal to voluntary assessment procedures on the national (e.g. “Avis Technique” in France) or European levels (European Technical Assessment accompanied by reference materials for the dimension and execution of appropriate works). This specific technical assessment work also contributes over the long term to the creation and revision of standards.

1.2 Problem of insurability

Insurance companies analyse and insure structures based on the risks they may pose to user safety as well as their durability given the construction processes, innovative or not, used to create them.

The texts used as a basis for this analysis are of a regulatory nature and should be imposed on all actors, for some, or are formal texts arising from expert consensus, for others.

The products and processes that fall under the specifications in these texts are considered to be *common techniques*, and therefore pose a normal risk. They should not be limited in their insurability as long as they are approved by the insurance companies as fit for use within the field of application.

Other products and processes fall within *non-conventional techniques* and are therefore subject to a specific procedure by insurance companies for the establishment of insurance contracts in line with the French law of 4 January 1978, commonly called the “Spinetta law”.

1.3 Durability assessment details

While the assessment process may be perceived as complex, any durability assessment methodology such as the one proposed should offer a clear vision of the existing possibilities. It should cover new cementitious materials (new concretes, new concrete products, new constituents, etc.). Because not every topic can be addressed, this letter provides clarifying information specifically about durability assessment.

The example showcased here was launched by Lafarge (today LafargeHolcim). This work is the outcome of a French working group, which included CSTB, in charge of “Assessment” and Lafarge interested in “Technological innovation” with the support of CERIB and CEREMA, especially for their expertise in assessing durability of target materials and for reference materials to normative work.

2 General process

A durability assessment methodology should guide an applicant and an assessor as they begin to assess the durability of new cementitious materials. The various possible cases should first be reviewed to assess whether these products fall within a normative framework or not.

In particular, the methodology should be designed for industrial and assessment bodies. It should aim to provide technical elements that will:

- assist in the identification the risks to which these products may be exposed
- help define the consequences of these risks for future material properties
- help select or develop assessment methods to quantify the consequences of the risks specific to each new product.

The standards that the applicant may refer to are listed in section 3. The various national and European assessment procedures are described in section 0. In terms of durability assessment methodology, there is no single assessment solution because of the multiplicity of aspects of new products or systems within the building sector. When an assessment procedure begins, part of the work done by the organisations in charge of the assessment is to build the assessment framework to be used before marketing the product. For example, it may be necessary to adapt testing methods to the material being assessed and to its planned field of application.

Applicants should have as clear an idea as possible of how their invention will be assessed. This helps to optimise discussions between the applicants and assessment body. It is also important to inform a potential applicant of how they can test their invention starting in the development phase before any formal assessment request, which may result in application failure if the assessment method has not been properly adapted. The proposed method (see section 4) may also apply to solutions that are technological breakthroughs as well as to other more traditional products. Potential applicants are advised to contact an assessment body as early as possible.

The process showcased here relies on thematic fact sheets (see online [supplementary material](#)) that address different kinds of alterations as well as the main tests currently used to assess the gravity of their consequences. Using these fact sheets, the different parties will be able to create their own assessment strategy, chose among proposed tests, decide to use a variant, or even design new tests that are as relevant as possible to the properties to be assessed.

3 The current regulatory context (October 2015)

This document was written to reflect the current documents published on concrete and cement product durability in a regulatory context.

The standardisation context for concrete structural applications is briefly summarised in Fig. 1. Other representations of this context are available in standards EN 206 [1] and EN 13670 [2]. The construction of concrete building structures relies on a coherent set of texts that cover the requirements that must be met, product performance, product manufacturing conditions, and integration into the structure, as well as design and process

factors. For some applications, standards list very precise requirements for the finished product, including durability requirements. For others, standards refer generally to texts that contain shared requirements, such as standards EN 206 [1] and EN 13369 [3].

For applications that fall under standards EN 206 [1] and EN 13369 [3], creating durability performance depends mostly on composition specifications for each exposure class (additional criteria based on "guides" or "recommendations" may be requested in addition to the specifications documents). In France, the use of performance-based methods is not fully integrated into the existing regulations. As needed, the FD CEN/TR 16563 [4] documentation booklet "Principles of the equivalent durability procedure" provides guiding principles for creating an equivalent durability procedure. The application of this procedure requires a national application document (NAD) that does not currently exist in France. The results of the PERFDUB French national project may become the underlying structure for such a future document. The main goal of PERFDUB is to define a methodology on the national scale to assess concrete durability (and that of concrete structures) using a performance-based approach that includes both the "absolute" and "comparative" methods [5].

Non-conventional product assessment procedures

Innovative building products and systems sometimes fall outside of the scope of current regulations. In this case, the developer can appeal to technical assessment procedures that will help get products on the market in France or Europe. There are two large families of procedures that can be distinguished: national voluntary procedures and European procedures that are governed by Construction Products Regulation (CPR). Below, we describe the main French procedures, ETPM (Preliminary Material Technical Assessment), ATE_x (Experimental Technical agreement), and ATE_c ("Avis Technique" or technical agreement) and the European procedure, ETA (European Technical Assessment). These procedures include product durability assessment based on the target field of application. They are carried out

in France by CSTB for the building sector and by CEREMA for the civil engineering sector.

ETPM applies to non-standard construction materials or semi-products. These materials and semi-products are constituents of finished products or systems that will be used in constructions (ex.: cement for making prefabricated concrete products, glass plates for making windows). The manufacturer of these materials generally does not have a direct relationship with the constructor. The final field of application is generally broad and insufficiently defined.

ETPM are carried out at the request of manufacturer on a voluntary basis. They are not covered by regulations.

The goal of ETPMs is to examine and summarise the most relevant pieces of evidence that a product suits a planned field of application, often with a wide scope. ETPM assess the characteristics of a material or semi-product. They do not assess the suitability for use since the product or procedure and the associated field of application are not clearly defined. The document is drawn up jointly by CSTB and the requester. It has two parts: the technical file prepared by the requester and the technical assessment itself prepared by CSTB. Processes created for the assessed innovative materials or semi-products are presumed to later be subject to Ate_x procedures and/or Avis Technique. That is why the document is submitted to a Specialised Group ("GS") of the technical agreement Commission, even though it is handled outside of the Avis Technique procedure.

ATE_x applies to innovative processes that do not yet have worksite references. It takes place before the "Avis Technique". ATE_x is made for limited application to a single construction operation that has already been identified or for a limited field of application for similar structures. The reviewed field is also narrower than the one for the Avis Technique. The procedure timeline is also shorter (two-three months). The "**Avis Technique**" is the most widely known and widely used technical assessment procedure. It is governed by a decree placing it under the supervision of a specific Commission (CCFAT).

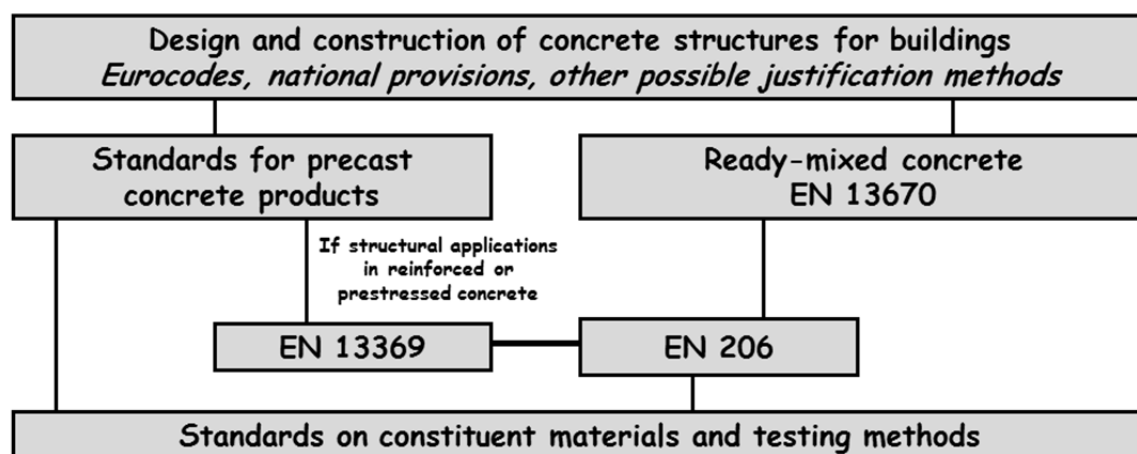


Figure 1. European standardisation context for concrete structures.

It is meant to provide all construction industry participants with an authorised opinion on new products, processes, and equipment for a specific use. It notably indicates the ways that the process or product:

- complies with current regulations
- is suitable for use in construction
- provides a known durability in service

These technical agreements are informational documents. They are not mandatory and they do not have any particular regulatory effect. They are created by technical experts working in Specialised Groups brought together by CCFAT.

The agreement has two parts: a technical file summary created by the requester and the opinion itself. It is delivered by CCFAT after examination by Specialised Groups (GS) named by this organisation.

CSTB examines the validity of the evidence in the request file submitted by the requester. The conclusions of this examination are presented to the Specialised Group in charge of creating the agreement. The agreement is then published by CSTB on its website.

The “Avis Technique” applies to new products, procedures, and equipment. Systems and structures whose components, characteristics, and implementation fall under conventional practices are not covered by this procedure.

For products with a CE marking, CCFAT may deliver an agreement in the form of a technical application document (DTA).

European Technical Assessment (ETA) is a European procedure. It is defined in regulation (EU) No. 305/2011 on construction products (CPR), which came fully into force on 1 July 2013. Its key new concept, the Declaration of Performance (DoP), is a new document that replaces the CE compliance declaration following the construction products directive (CPD). Based on the planned use(s) for its product, the manufacturer may choose the product's essential characteristics of which it wishes to declare the performance. Currently, to place construction products on the market that are covered by a harmonised standard, the manufacturer must issue a Declaration of Performance, then apply the CE marking to products that comply with the Declaration of Performance. For a product that is not (or is not entirely) covered by a harmonised standard, the manufacturer may request an ETE in order to obtain a Declaration of Performance and CE marking. The ETE is issued based on reference to the EAD (European Assessment Document). The EAD is issued jointly by all other relevant European technical assessment organisations before being adopted by EOTA (European Organisation for Technical Assessment: www.eota.eu). When the innovative product is part of a product family that has already received an EAD (quick setting cement, calcium sulfoaluminate cement, etc.) the provisions of this EAD must be taken into account.

The assessment of new products or systems is not fundamentally different from the approach taken in a regulatory context. For example, for a new product, characterisation generally includes composition, properties, and durability characteristics. Assessment methods for

innovative products may differ from regulatory methods in cases where, for example, it is necessary to quantify a new risk or a new property that is not covered in an existing standard. It is also sometimes necessary to adapt testing methods due to the particular properties of the proposed innovation. It is then the responsibility of the assessment body to approve the most relevant testing method.

4 Method for identifying risks and choosing which tests to carry out

Durability assessment includes several stages. The first two stages include describing the invention (see stage 1) and the properties whose durability is to be assessed for the planned field of application (see stage 2). The next stage involves making a list of the potential kinds of degradation (see stage 3). To do so, a list of the main kinds of degradation known for cementitious materials is proposed in this document. Concise thematic fact sheets describing these degradations are provided as online [supplementary material](#) to this document. According to the particular nature of a product or system, other types of degradation may be considered.

The applicant provides evidence that provide a way to qualify the durability over time of the product or system performance. Different means are available, such as lessons learned from the field and laboratory ageing tests (see stage 4). As for laboratory tests, criteria for test method selection and execution are proposed (see stage 5) as well as assessment criteria (stage 6). A method is proposed for cases where a specific method of alteration needs to be taken into account. Finally, the last stage for the assessment organisation is to give an overall assessment of the product's durability by compiling the different data available. It is especially important to take into account the exposure conditions and the lifespan of the structure in which the product will be used.

4.1 Stage 1: describing the invention

The goal of this stage is to give a detailed description of the innovation: the product composition, the field of application and the planned lifespan, the possible manufacturing specificities, implementation specificities, and any other information that might be useful to the assessment body.

This stage ensures whether the new product or system proposed is already covered by current standards in force (if so, the durability for the field of application and the planned lifespan are then presumed acquired) or the assessment of durability needs to be carried out.

4.2.1. The product

The following questions help to define the product and identify its particular characteristics:

- 1) How would you describe the product (constituents, mix design, geometry, ...)?
- 2) Does the product meet a standard?
- 3) Are the products constituents all standard-compliant or well described in a product standard?

- 4) If yes, do the combination and proportions of the constituents fall under a standard?
- 5) Is the formed cement matrix similar to those formed by conventional standardised binders (hydrate assemblage, porosity, etc.)?
- 6) Does the product have inclusions (aggregate, fibres) that are not conventional for cementitious materials?
- 7) Are the properties or characteristics of the final product standardised?

4.2.2. Field of application

The field of application is defined by answering the following questions:

- Is the field of application conventional?
- What are the main functions of the product?
- What is its planned lifespan?
- Is it planned to play a structural role?
- If yes, are its mechanical properties compatible with an existing approval method (Eurocodes, etc.) used for structural design?
- Is there a risk of incompatibility between the product and another constituent or material it might come into contact with?
- Are metallic elements used?
- What stresses are foreseen?
- What are the climate characteristics (temperature, relative humidity, freezing, etc.)?
- What are the chemical agents that might be in permanent or occasional contact with the product (natural water, salt, sulphates, acid...)?
- What are the other foreseen stresses (abrasion, permanent or cyclical mechanical loading)?
- Is the product in direct contact with the environment (protective cover)?

4.2.3. Implementation

Finally the standard implementation for this product must be described. These items inform the answers to the following questions:

- Are the implementation conditions conventional (like, for example, those specified by DTU 21 [6]) or are they unique?
- Is it necessary to certify product applicators?

4.2 Stage 2: properties to be verified

In all cases, the durability of mechanical stability properties must be verified. The applicants can also claim the durability of other properties if they so wish.

N.B.: Harmlessness to people (construction workers, users) and the environment at different stages in the products lifespan are not included in this guide, but must be assessed according to the regulations in force.

4.3 Stage 3: degradation risks

The inventory of degradation risks that would lead to significant performance loss must be an exhaustive list based on the product specificities, its use, and its planned environment. Table 1 is a tool to help with this inventory. It lists the known degradations for conventional concrete. It is also important to think of additional risks specific to the invention as needed.

The mechanisms for cementitious material alterations are often complex. These mechanisms are described in the example showcased here in thematic fact sheets (see online [supplementary material](#)) in order to provide a guide to understand them and decide if they need to be taken into account. These fact sheets cover the known potential degradation mechanisms for cementitious materials leading to a risk of loss of mechanical integrity. In the case of an alteration not covered by these fact sheets, a specific one may be created using the structure of those presented in this document.

Table 1. List of performance loss risks for the invention.

		Physiochemical degradation processes									
Properties		1- Corrosion of reinforcement induced by carbonation	2- Corrosion of reinforcement induced by chlorides penetration	3- Corrosion of other embedded metal elements	4- Expansion/Cracking during freeze/thaw cycles	5- Salt scaling during freeze/thaw cycles	6- Chemical damage (external sulphate reaction)	7- Expansion/cracking due to internal sulphate reactions	8- Expansion/ cracking due to alkali-silica reactions	9- Chemical damage (acidic surroundings)	10- Other *?
		Y/N?	Y/N?	Y/N?	Y/N?	Y/N?	Y/N?	Y/N?	Y/N?	Y/N?	Y/N?
	Mechanical integrity	Y/N?	Y/N?	Y/N?	Y/N?	Y/N?	Y/N?	Y/N?	Y/N?	Y/N?	Y/N?
	Other properties	Y/N?	Y/N?	Y/N?	Y/N?	Y/N?	Y/N?	Y/N?	Y/N?	Y/N?	Y/N?

Y: Risk to be taken into account.

N: Not applicable. * for example, it may be an issue of dimensional instability due to contact with water.

This approach may also be used to describe changes in other properties. For example, dimensional instability leading to material cracking in its environment might be considered.

The structure of the pathology sheets is as follows:

- 1) Introduction
- 2) Consequences
- 3) Physico-chemical mechanisms
- 4) Main models
- 5) Main parameters
- 6) Testing method stages
- 7) Reference testing methods
- 8) Performance assessment
- 9) References

4.4 Stage 4: evidence for the assessment

Assessing the consequences of an identified risk can rely on:

- qualification tests described in section 4.5 below
- lessons learned from the field (existing structures or test specimens)
- results of previous tests (technical documents, publication)
- an analysis of physio-chemical mechanisms (see sections 3 and 4 of the pathology sheets)
- calculation results
- etc.

4.5 Stage 5: testing methods for each property-degradation mode couple

An approach for selecting relevant laboratory tests is provided below and illustrated in Fig. 2:

- 1) The first step involves checking if there is a relevant test in the current provisions in force for the area of use to assess this durability. If that is the case, this test must be preferred. A non-exhaustive list of possible tests is given in the thematic fact sheets; see "reference testing methods" in online [supplementary material](#).
- 2) If that is not the case, it is possible to adapt a relevant reference test as long as the principle of the test is not undermined. Changes to testing conditions must be minor and may not modify the degradation mechanisms being studied. It is important to consult section 5 "Main parameters" on the fact sheets to determine what testing conditions might be adapted.
- 3) If neither of the two previous solutions is possible, a test developed and used by a single laboratory may be used, for example. This test should be suitable and credible. Section 7 of the fact sheets also proposes specific and documented tests.
- 4) Finally, as a last resort, a new test must be proposed. This test may be created using the pathology sheets based on "physio-chemical mechanisms" (section 3) and "main parameters" (section 5). This new test must be described exhaustively.
- 5) Tests must be carried out using the selected method.

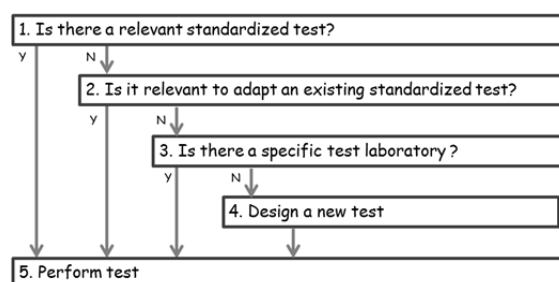


Figure 2. proposed approach for choosing which laboratory tests to carry out

4.6 Stage 6: assessment method

The goal of this section is to identify the different available methods for reaching a conclusion about the product or system ability to maintain its properties.

Two main methods are possible [1,4]: "Absolute" approach and "Comparative" approach. The "absolute" approach is based on a comparison between threshold values and measured values using the same testing methods for both measurements to establish a performance level. There are two possible choices:

- 1) Ideally, it is best to use the threshold values available in the existing provisions in the place of use. Section 7 of the fact sheets lists technical documents. These documents list thresholds in some cases.
- 2) As a second choice, the threshold values defined in the calculation methods may be used. Section 4 of the fact sheets lists the main models.

The "comparative" approach is based on a comparison between measured values derived from the product and from a reference material. It is important to make the reference material choice explicit. Note that it is advisable to take account of uncertainties of test results.

Finally, it is important to come to a conclusion on the conformity of the invention to the description provided by the applicant as well as to establish whether there are no non-compliances.

Acknowledgements

The authors would like to thank Michel Delort and Laurent Izoret, chairs of CEN/TC51 (Cement and Construction Lime) standardisation committee, for their contribution to the working group and to the creation of this document.

The authors would also like to thank the following editors for the significant improvements they made to this document: Charles Baloche, CSTB, Francois Boutin, CSTB, Anca Cronopol, CSTB, David Henriques, CSTB, Yannick Lemoigne, CSTB, Nicolas Ruaux, CSTB, Remi Barbarulo, LafargeHolcim R&D, Eric Brouard, LafargeHolcim R&D, Francois Delarrard, LafargeHolcim R&D, Edouard Gengembre, LafargeHolcim R&D, Gabriel Pham, LafargeHolcim R&D, François Jacquemot, CERIB, Jonathan Mai-Nhu, CERIB, Marjorie Petitpain, CERIB

References

- [1] NF EN 206:2014. Concrete - Specification, performance, production and conformity, 2014.
- [2] NF EN 13670:2013 Execution of concrete structures, 2013.
- [3] NF EN 13369:2013. Common rules for precast concrete products, 2013.
- [4] FD CEN/TR 16563:2014. Principles Of The Equivalent Durability Procedure, 2014.
- [5] Irex, The National Research Project PERFDUB, 2015, <http://www.perfdub.fr/en/>.
- [6] NF P18-201:2004. DTU 21 - Building works - Execution of concrete works - Technical specifications, 2004.

Supplementary material

Durability performance assessment of non-standard cementitious materials for buildings: a general method applied to the French context

Fact sheet 1 - Risk of steel corrosion induced by carbonation

Pierre Pimienta^a, Blandine Albert^b, Bruno Huet^{b*}, Michael Dierkens^c, Philippe Francisco^d,
Patrick Rougeau^d

^a Université Paris-Est, CSTB, 84 avenue Jean Jaurès Champs-sur-Marne, 77447 Marne-la-Vallée Cedex 2, France

^b LafargeHolcim R&D, 95 rue du Montmurier, 38291 Saint-Quentin-Fallavier Cedex, France

^c CEREMA, 25, avenue François Mitterrand - CS 92 803, 69674 Bron Cedex, France

^d CERIB, 1 Rue des Longs Reages, 28230 Épernon, France

Received: 30 September 2016 / Accepted: 05 December 2016 / Published online: 28 December 2016
© The Author(s) 2016. This article is published with open access.

1 Introduction

This risk concerns concrete reinforced with ordinary black steel that is exposed to humid atmospheres.

The risk of corrosion by carbonation results from two successive physiochemical mechanisms. The first is concrete carbonation, which lowers pH. Carbonation occurs more or less quickly through the concrete cover depending on the concrete thickness and composition. The second is the active corrosion of steel that follows the dissolution of the passivation layer once low pH levels have reached the reinforcements. The development of corrosion requires a certain humidity level (reinforced materials in a constantly dry environment are not at risk).

2 Consequences

- Cracking, spalling of the concrete cover.
- Loss of bond between concrete and reinforcement.
- Reduction of reinforcement cross-section, leading to a loss of load-bearing capacity of the reinforced structure (ultimate state).

3 Physiochemical mechanisms

With Portland cement-based conventional concrete, reinforcements are passivated by the typically high pH of the interstitial pore solution (12.5 to 13.5). This passivation is compromised when the pH around the reinforcements drops sharply (pH < 10-11). This drop in pH is observed when the concrete cover is completely carbonated [1].

Concrete carbonation:

- Carbonation is a series of hydrate reactions (CH, C-S-H, etc.) between the cement paste and atmospheric carbon dioxide (Fig. 1).
- CO_{2(g)} penetrates by diffusion through non-saturated pores. Some of the CO_{2(g)} dissolves into the interstitial solution, where it may react with hydrates.
- When portlandite is present, it is the first hydrate to be carbonated. However, over time, each hydrate in concrete may be carbonated, ultimately forming a mix of carbonates, silica and alumina gel, and liberating water. These phases do not affect binding properties.

* Corresponding author: Bruno Huet, LafargeHolcim R&D, 95 rue du Montmurier, 38291 Saint-Quentin-Fallavier Cedex, France, bruno.m.huet@lafargeholcim.com

- The dissolution of hydrates and the formation of calcium carbonate, CaCO_3 , occur rapidly compared to mass transfer processes. This leads to a steep carbonation front.
- The pH of the pore solution drops below 9, which is why the carbonated crust can be identified with a coloured indicator (Fig. 2a).

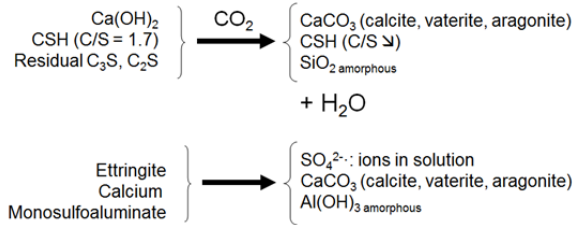


Figure 1. Typical carbonation reaction of hydrates, nature of reactions may change with the nature of initial hydrate phases.

- The apparent rate of concrete carbonation depends on the $\text{CO}_{2(g)}$ diffusivity and the amount of "carbonatable" hydrates (Fig. 2b):
- The quantity of carbonatable hydrates rises with the degree of hydration, the quality of the cure, and the cement content and composition.
- The maximum conversion degree from hydrates into CaCO_3 falls along with relative humidity. These reactions cannot take place in the absence of liquid water (see red line in Fig. 2b).
- The carbon dioxide diffusion rate decreases when the cement matrix is more compact.
- The carbon dioxide diffusion decreases when water saturation in the pores increases.
- Higher $\text{CO}_{2(g)}$ concentrations increase the apparent rate of carbonation and they can influence the nature of the newly formed phases.

Steel corrosion in carbonated concrete:

Reinforcement corrosion is a set of electrochemical reactions between the iron in the reinforcements and the atmospheric oxygen in presence of water. In the absence of chlorides, the rate of corrosion becomes significant only after concrete carbonation and after the pH drop of the interstitial solution. This rate is influenced by two simultaneous processes, oxygen transport and iron oxidation:

- The diffusion rate of gaseous oxygen is also related to the microstructure of the carbonated concrete, it decreases with increasing water content.
- The electrochemical reaction rates at the interface between reinforcement and concrete increase in line with the humidity present in the material.

The water saturation level in the porosity of concrete, which depends on relative humidity, determines the optimum carbonation and corrosion rates for each of the two processes (see Fig. 2b). Water content is influenced by water mass transfer properties (capillary flow and vapour diffusion), by the water absorption capacity of the porous

network, and by climatic conditions (relative humidity, rain, wind, sun). In very dry or humid environments, corrosion rate is quite low.

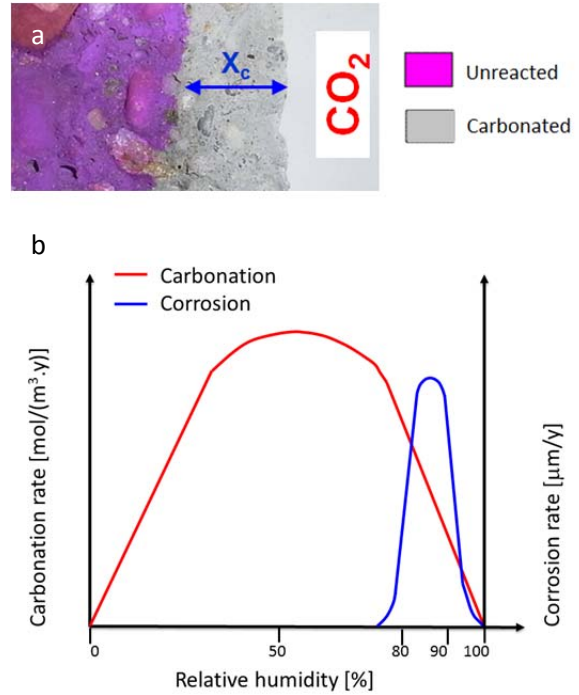


Figure 1. Carbonation depth measurement using a coloured indicator (a) and carbonation and corrosion rates based on relative humidity (b).

Corrosion leads to the creation of an expansive oxide layer on the surface of the steel. This expansion causes internal stresses that can lead to cracking of concrete around the reinforcement. Cracks that reach the surface of concrete significantly accelerate the diffusion of oxygen, carbon dioxide, and water.

This second stage of the phenomenon, the corrosion of the reinforcements themselves, is generally not taken into account when designing structural performance. Nevertheless, it may be taken into account if very low corrosion rates are justified

4 Main models

As of 2015, there is no complete standardised model for prediction carbonation depth in concrete (x_c), although several models have been published.

The Papadakis AIChE 1989 [2] model is an example of an analytic model to analyse carbonation depth x_c in laboratory test in constant atmospheric conditions over time (t):

$$D_a = \frac{D_g \cdot C_{\text{CO}_2,g}}{C_{\text{Ca,S}}} \quad (1)$$

$$x_c = \sqrt{D_a} \sqrt{t} \quad (2)$$

where D_a is the apparent diffusion coefficient in the carbonated front, D_g is the CO_2 diffusion coefficient in the

carbonated layer, $C_{CO_2,g}$ is the CO_2 concentration in the atmosphere, and $C_{Ca,s}$ is the total calcium concentration in the carbonatable hydrates per volume of concrete. Numerical models have also been published [3-5] that incorporate variable relative humidity in the environment and even simultaneous drying of the material. The relationship with on-site behaviour can be established with models like *fib* Model Code [6]. The reader may refer to J. Mai-Nhu's thesis [7] for a more exhaustive review of existing models.

5 Main parameters

Material parameters:

- Material transport properties.
- The amount of carbonatable material in the product (the amount of portlandite in particular).
- Curing length and conditions. A moist and sufficiently long cure creates a well-hydrated product with reduced porosity and transport properties.

Environment parameters:

- Relative humidity, rain, cycle, wind, sun exposure, and temperature: these parameters influence the concrete drying rate as well as hydration rate.
- Ambient atmospheric CO_2 and O_2 concentration.

6 Testing method stages

Testing methods involve exposing samples to a given relative humidity and partial pressure CO_2 .

The key stages are:

- Curing length and conditions (temperature, under water, in a watertight bag or at 100% RH).
- Length and conditions of initial drying (T, RH). This stage helps reducing the water content of concrete and thereby accelerating CO_2 diffusion. The duration of this drying step may not be enough to create a homogeneous water content profile.
- Duration and conditions for the carbonation test itself (T, RH, $\%CO_{2(gaz)}$).
- At selected time intervals, the carbonation front is highlighted by spraying a 0.5% phenolphthalein solution on a fresh cross-section, which is perpendicular to the CO_2 penetration surfaces.

The important quantities of interest are carbonation depth after a given time period or the apparent diffusion coefficient of the carbonation front (see section 4).

N.B.: pure phenolphthalein (CAS No. 77-09-8) is classified as a CMR product (Carcinogenic, Mutagenic, Reprotoxic) in category 1B (strong presumption (conclusive animal tests)) and it must be used in a professional context in line with the regulations in force. Ordering a 0.5% phenolphthalein solution from a supplier avoids having to handle this substance in its pure state. The solution is diluted enough to avoid classification as a CMR product. There are also other products that may be used as substitutes.

7 Reference testing methods

Tests listed in national regulations valid in place of use for conventional concrete:

Name	Cure	Drying	Carbonation	Duration	Comment
DD CEN/TS 12390-10: 2007 [8]	Under water until C_s reaches half of targeted C_s	-	natural $[CO_2]$ RH=65%	2 years	Used in CUAPs.
EN 13295:2004 [9]	Under water, unspecified duration	-	$[CO_2]=1\%$ RH=55%	> 80 d	Test for repair mortar.
XP P18-458: 2008 [10]	Under water 2 d	14 d, 45°C	$[CO_2]=50\%$ RH=55%	44 d	
Cur - Recommendation 48 [11]	Under water 3 d	-	$[CO_2]=2\%$ RH=65%	Between 91 d and 365 d	
GBJ82-85 [12]	In air 28 d RH=70%. T=20°C	-	$[CO_2]=20\%$ RH=70%	56 d	
ISO/DIS 1920-12: 2014 [13]	Under water 28 d	14 d, RH=50-70%	$[CO_2]=3\%$ RH=55% T=22°C	70 d	

Alternative test:

Fpr CEN/TS 12390-12: 2012 [14]	Under water 28 d	14 d RH=50-65% T=20°C	$[CO_2]=4\%$ RH=55%	112 d	Proposed standard (pending)
--------------------------------	------------------	-----------------------	---------------------	-------	-----------------------------

Carbonation depth can be measured using standards NF EN 14630:2007 [15] or RILEM CPC 18 [16]. Based on carbonation depth measurements at dates, the diffusion rate of the carbonation front can be calculated (see section 4).

8 Performance assessment

Assessment method:

- *comparative assessment*: the carbonation depth is measured on the candidate concrete, then is compared to the values obtained from a standardised reference product using the same testing method.
- *absolute assessment*: currently, there is no absolute threshold value that has been defined for the testing methods.

References

- [1] J.-P. Ollivier, A. Vichot, La durabilité des bétons, ATILH, 2008.

- [2] V.G. Papadakis, C.G. Vayenas, M.N. Fardis, A reaction engineering approach to the problem of concrete carbonation, *AIChE J* (1989) 35: 1639-1650. <https://doi.org/10.1002/aic.690351008>
- [3] B. Bary, A. Sellier, Coupled moisture-carbon dioxide-calcium transfer model for carbonation of concrete, *Cem Concr Res* (2004) 34: 1859-1872. <https://doi.org/10.1016/j.cemconres.2004.01.025>
- [4] T. Ishida, C.-H. Li, Modeling of carbonation based on thermo-hygro physics with strong coupling of mass transport and equilibrium in micro-pore structure of concrete, *J Adv Concr Technol* (2008) 6: 303-316. <https://doi.org/10.3151/jact.6.303>
- [5] M. Thiery, G. Villain, P. Dangla, G. Platret, Investigation of the carbonation front shape on cementitious materials: Effects of the chemical kinetics, *Cem Concr Res* (2007) 37: 1047-1058. <https://doi.org/10.1016/j.cemconres.2007.04.002>
- [6] fib bulletin 34, Model Code for Service Life Design, 2006.
- [7] J. MAI-NHU, Corrosion des armatures du béton : couplage carbonatation/chlorures en présence de cycles hydriques Université Toulouse III - Paul Sabatier, 2013.
- [8] DD CEN/TS 12390-10:2007. Testing hardened concrete - Part 10: Determination of the relative carbonation resistance of concrete, 2007.
- [9] NF EN 13295:2004. Produits et systèmes pour la protection et la réparation des structures en béton - Méthodes d'essai - Détermination de la résistance à la carbonatation, 2004.
- [10] XP P18-458:2008. Essai pour béton durci - Essai de carbonatation accélérée - Mesure de l'épaisseur de béton carbonaté, 2008.
- [11] CUR-aanbevelingen 048:2010 Procedures, criteria en beproevingsmethoden voor de toetsing van de geschiktheid van nieuwe cementen voor toepassing in beton en voor de gelijkwaardige prestatie van beton met vulstoffen, 2010.
- [12] GBJ 82-85 Standard for test methods of long-term performance and durability of ordinary concrete, 1986.
- [13] ISO/DIS 1920-12:2014. Essais du béton - Partie 12 : détermination de la résistance du béton à la carbonation - Méthode de carbonation accélérée, 2014.
- [14] ONR CEN/TS 12390-12:2010. Testing hardened concrete — Part 12: Determination of the potential carbonation resistance of concrete: Accelerated carbonation method, 2010.
- [15] NF EN 14630:2007. Produits et systèmes pour la protection et la réparation des structures en béton - Méthodes d'essais - Mesurage de la profondeur de carbonatation d'un béton armé par la méthode phénolphthaléine, 2007.
- [16] RILEM, CPC-18 Measurement of hardened concrete carbonation depth, *Mater Struct* (1988) 21: 453-455. <https://doi.org/10.1007/BF02472327>

Supplementary material

Durability performance assessment of non-standard cementitious materials for buildings: a general method applied to the French context

Fact sheet 2 - Risk of steel corrosion caused by chloride ions

Pierre Pimienta^a, Blandine Albert^b, Bruno Huet^{b*}, Michael Dierkens^c, Philippe Francisco^d,
Patrick Rougeau^d

^a Université Paris-Est, CSTB, 84 avenue Jean Jaurès Champs-sur-Marne, 77447 Marne-la-Vallée Cedex 2, France

^b LafargeHolcim R&D, 95 rue du Montmurier, 38291 Saint-Quentin-Fallavier Cedex, France

^c CEREMA, 25, avenue François Mitterrand - CS 92 803, 69674 Bron Cedex, France

^d CERIB, 1 Rue des Longs Reages, 28230 Épernon, France

Received: 30 September 2016 / Accepted: 05 December 2016 / Published online: 28 December 2016
© The Author(s) 2016. This article is published with open access.

1 Introduction

This risk affects concrete with metallic reinforcements made from ordinary steel, which are exposed to environments with high chloride ion contents (marine environments, de-icing salts, water rich in chloride (pools), etc.). When the metal reinforcements reach a critical chloride ion concentration threshold, they can undergo pitting corrosion.

2 Consequences

- Cracking, spalling of the concrete cover.
- Loss of bond between the reinforcement and the concrete, reduction of reinforcement length, leading to a loss of load-bearing capacity in the reinforced structure (in the worst case scenario).

3 Physiochemical mechanisms

The mechanisms described below are those known for Portland cement based concrete, where the cover has not been modified by other kinds of attack. For different chemical compositions or for materials that have been

noticeably affected by carbonation or other factors, certain mechanisms are to be detailed further.

With Portland cement-based conventional concrete, reinforcements are passivated by the generally high pH of the interstitial solution (12.5 to 13.5) and by the low initial chloride content of the concrete after production [1]. Chloride corrosion is caused by two successive physiochemical mechanisms.

The first mechanism is the penetration of chloride ions into concrete, from the surface exposed to the steel (see Fig. 1a). This happens more or less quickly depending on the thickness and the transport properties of the concrete, as well as the surrounding environmental conditions (the mechanisms involved are described below).

The second mechanism is the active corrosion of steel; once the "critical" chloride content threshold is reached adjacent to the reinforcements (the scientific community is still debating the actual value of this critical threshold). This second phase is characterised by the loss of the passive layer's protective capacity and by significant reinforcement corrosion rate. After an initial phase, the corrosion propagates under certain conditions (described below) and it can lead to more or less significant damage (see Fig. 1b)

* Corresponding author: Bruno Huet, LafargeHolcim R&D, 95 rue du Montmurier, 38291 Saint-Quentin-Fallavier Cedex, France, bruno.m.huet@lafargeholcim.com

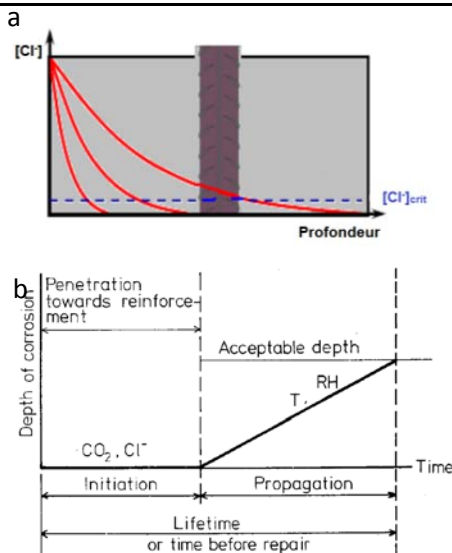


Figure 1. Changes in chloride concentration as a function of time and depth (a) and the different phases of steel corrosion according to Tuutti [2] (b).

Initiation phase: chloride ion penetration into cement materials.

Chloride ion penetration into concrete is influenced by two simultaneous processes:

- the transport of free chloride ions through the concrete cover:
 - by diffusion, this mode of transportation is more favoured when the material is saturated with water.
 - by advection, this mode of transportation is more favoured when there are frequent saturation/drying cycles, such as for concrete in tidal or splash zones.
- chloride fixation by hydrates:
 - on the surface adsorption of C-S-H.
 - into the crystal network by the formation of Friedel's salt.
 - only chloride ions that are unbound to the matrix and remain free in solution can diffuse and play an active role in rebar depassivation and active corrosion.
- Overall, the apparent penetration rate of these chloride ions into the concrete depends on their diffusivity in the material and on the amount of hydrates that is available to bind them. This amount rises with the degree of hydration, the quality of the cure, and the cement content.

Propagation Phase: steel corrosion in concrete in the presence of chloride ions.

Reinforcement corrosion results from a set of electrochemical reactions between the iron in the reinforcements and atmospheric oxygen in the presence of water. The corrosion rate becomes significant only after the critical chloride content threshold is reached against the steel. Only free chlorides are active in the depassivation and active corrosion processes. This is influenced by two

simultaneous processes, oxygen transport and iron oxidation.

- The rate of diatomic oxygen diffusion is also based on the micro-structure of concrete; it decreases with an increase of water content.
- The electrochemical reaction rates between the reinforcements and the concrete increase with water content.

Overall, corrosion rate becomes significant in the presence of humidity and oxygen, with the optimum falling between 80-95% relative humidity.

Comments

The "Critical" chloride content ($[Cl^-]_{crit}$) is the amount of chloride above which the passivation layer is compromised. From an operational point of view, the thresholds refer to total chloride content and are expressed in relation to a quantity of Portland cement or in relation to the mass of the concrete (for information purposes, the standard limits in EN 206 are 0.4% of the concrete mass for conventional reinforced concrete, and 0.1% for concrete with prestressed concrete).

For a cement material with a chemistry that is very different from Portland cement, the critical chloride threshold value may not be known.

Chloride-induced corrosion does not lead to generalised corrosion, as is the case with carbonation. Rather, the metal is attacked locally in specific areas, or pits, where there is a high rate of iron dissolution.

The service life of a structure generally depends on the initial phase, i.e. on how long it takes for chloride ions to penetrate the structure until their concentration reaches the critical threshold at the steel depth. Nevertheless, the propagation phase described in the fact sheet "Corrosion of metallic elements" can be included in a structure's lifespan if a very low rate of active corrosion can be justified.

4 Main models

As of 2015, there is no complete standardised model for predicting the penetration of Cl^- ions in a cement product, although several prediction models have been published.

The AFGC 2004 guide [3] proposes two different kinds of model:

- *Empirical models*: the change in chloride ion concentration in the concrete cover over time is predicted by resolving Fick's second law with the Error function (examples: Life 365 model available online or the Duracrete model, updated in the fib Model Code [4]) after setting the apparent diffusion coefficient based on the results of laboratory tests.
- *Physical models*: ion transport and interactions are described using equations based on physical mechanics. For example, the LERM model [5] works in saturated conditions, Stadium [6] is able to predict behaviour in a partially saturated medium, and SDRaM-CRETE [7], the CERIB model, estimates

lifespan based on when chloride-induced reinforcement corrosion begins, on carbonation, and on the interaction between these two phenomena in a partially saturated medium, by including variability.

- the flow of penetrating chloride ions for a test in a permanent state,
- the electric conductivity.

Most of these models use a diffusion coefficient that has been determined in a laboratory in saturated conditions, or that has been properly assessed based on the concrete's composition, when this composition is conventional. Some models can include diffusion coefficients that change over time due to hydration.

Influential parameters

Material parameters:

- Transportation properties of the concrete (absorption, diffusivity, etc.).
- Capacity of the cement paste to bind chlorides with hydrates.

Environment parameters:

- Accelerated chloride penetration in the presence of wetting/drying cycles.
- Temperature.
- Cl^- and O_2 concentration in the external environment.

5 Testing method stages

Laboratory tests generally involve establishing the diffusion coefficient for chloride ions in concrete. The main stages are:

- preliminary curing,
- possible pre-conditioning (saturation in a vacuum with a diluted soda solution, for example),
- the Cl^- ion penetration stage, for which several modalities are available:
 - diffusion in a saturated environment, the penetration of chloride ions is accelerated due to their high concentration and the test therefore lasts several months,
 - migration in a saturated environment in presence of an electric field; the test duration can be reduced to a few days, only,
- for each mode of ion transport in concrete, two states are possible:
 - a *transient* state, i.e. the chloride ion penetration front has not crossed the entire concrete sample,
 - a *steady* state, i.e. the chloride ion penetration front has penetrated the concrete entirely, and the concentration gradient between the two areas is maintained at a constant as a stationary flow.

The measured quantities of interest may be:

- the penetration front for a test in an electric field in a transient state,
- the concentration profile for a pure diffusion test in a transient state,

6 Testing reference points

Name	Cure	Conditions	Acceleration	Test duration	Comment
Pr CEN/TS 12390-11: 2010 [8]	28 d moist cure	Transient state. One of the sample's faces is submerged in a 30g/l NaCl solution	-	91 days.	Diffusion coefficient calculated with [Cl] concentration
ASTM C 1556a: 2011 [9]	28 d moist cure	Transient state. One of the sample's faces is submerged in a 150g/l NaCl solution	-	35 days.	Diffusion coefficient calculated with [Cl] concentration
NT Build 443: 1995[10]	28 d moist cure	Transient state 165 g/l NaCl solution	-	35 days.	Diffusion coefficient calculated with [Cl] concentration
XP P18-462: 2012[11]	91 d moist cure	Transient state. Concrete disc placed between two compartments containing a (0.1M NaOH + 0.5 or 1M NaCl et 0.1M NaOH) solution.	Migration in an electric field (20-30 V)	24 hours or more depending on the concrete.	Apparent diffusion coefficient calculated based on the penetration front [Cl].
XP P18-461: 2012[12]	91 d moist cure	Steady state. Set-up identical to XP P 18-462	Migration in an electric field (20-30 V)	At least 7 days	Effective diffusion coefficient calculated based on flow
NT Build 492: 1999 [13]	91 d moist cure	Transient state. Specific set-up. 100g/kg NaCl (cathode) and 12 g/l NaOH (anode)	Migration in an electric field (10 to 60V)	Between 6 hours and 3 days.	Apparent diffusion coefficient calculated based on the penetration front [Cl].
NT Build 355: 1997 [14]	91 d moist cure	Steady state, concrete disc placed between two compartments containing a (100g/kg NaCl, 12 g/l NaOH) solution	Migration in an electric field (12V)	At least 7 days	Effective diffusion coefficient calculated based on flow
(RCPT) ASTM C 1202 :2012 [15], AASHTO T277 [16]	28 d moist cure	Transient state, concrete disc placed between two compartments containing a (3% NaCl, 0.3N NaOH) solution.	Migration in an electric field (60V)	6	Conductivity measurement

7 Performance assessment

Assessment method:

- *comparative assessment*: the quantity of interest is measured on the candidate concrete, and then is compared to the values measured from a product meeting standard requirements and using the same testing method.
- *absolute assessment*: currently, there is no absolute threshold value that has been agreed upon for the testing methods listed in section 7.

References

- [1] J.-P. Ollivier, A. Vichot, La durabilité des bétons, ATILH, 2008.
- [2] K. Tuutti, Corrosion of Steel in Concrete, Department of Building Materials, Royal Institute of Technology, Stockholm, 1982, 469.
- [3] AFGC, Conception des bétons pour une durée de vie donnée des ouvrages. Maîtrise de la durabilité vis-à-vis de la corrosion des armatures et de l'alcali-réaction., Etat de l'art et Guide pour la mise en oeuvre d'une approche performantielle et prédictive sur la base d'indicateurs de durabilité, 2004.
- [4] fib bulletin 34, Model Code for Service Life Design, 2006.
- [5] O. Houdusse, H. Hornain, G. Martinet, Prediction of long term durability of Vasco Da Gama Bridge in Lisbon (SP 192-63), 5th CANMET/ACI International Conference on Durability of Concrete, Barcelona, 2000.
- [6] E. Samson, J. Marchand, Modeling the transport of ions in unsaturated cement-based materials, Comp Struct (2007) 85: 1740-1756. <https://doi.org/10.1016/j.compstruc.2007.04.008>
- [7] J. MAI-NHU, Corrosion des armatures du béton : couplage carbonatation/chlorures en présence de cycles hydriques, Université Toulouse III - Paul Sabatier, 2013.
- [8] XP CEN/TS 12390-11:2010 Essai sur béton durci - Partie 11 : détermination de la résistance du béton à la pénétration des chlorures, diffusion unidirectionnelle, 2010.
- [9] ASTM C 1556a:2011. Standard Test Method for Determining the Apparent Chloride Diffusion Coefficient of Cementitious Mixtures by Bulk Diffusion, 2011.
- [10] NT BUILD 443:1995. CONCRETE, HARDENED: ACCELERATED CHLORIDE PENETRATION, 1995.
- [11] XP P18-462:2012. Essai sur béton durci - Essai accéléré de migration des ions chlorure en régime non-stationnaire - Détermination du coefficient de diffusion apparent des ions chlorure, 2012.
- [12] XP P18-461 Juin 2012. Essai sur béton durci - Essai accéléré de migration des ions chlorure en régime stationnaire - Détermination du coefficient de diffusion effectif des ions chlorure, 2012.
- [13] NT BUILD 492:1999. CONCRETE, MORTAR AND CEMENT-BASED REPAIR MATERIALS: CHLORIDE MIGRATION COEFFICIENT FROM NON-STEADY-STATE MIGRATION EXPERIMENTS, 1999.
- [14] NT BUILD 355:1997. CONCRETE, MORTAR AND CEMENT BASED REPAIR MATERIALS: CHLORIDE DIFFUSION COEFFICIENT FROM MIGRATION CELL EXPERIMENTS, 1997.
- [15] ASTM C 1202:2012. Standard Test Method for Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration, 2012.
- [16] AASHTO T277:2007. Standard Method of Test for Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration, 2007.

Supplementary material

Durability performance assessment of non-standard cementitious materials for buildings: a general method applied to the French context

Fact sheet 3 - Risk of corrosion of metallic elements

Pierre Pimienta^a, Blandine Albert^b, Bruno Huet^{b*}, Michael Dierkens^c, Philippe Francisco^d,
Patrick Rougeau^d

^a Université Paris-Est, CSTB, 84 avenue Jean Jaurès Champs-sur-Marne, 77447 Marne-la-Vallée Cedex 2, France

^b LafargeHolcim R&D, 95 rue du Montmurier, 38291 Saint-Quentin-Fallavier Cedex, France

^c CEREMA, 25, avenue François Mitterrand - CS 92 803, 69674 Bron Cedex, France

^d CERIB, 1 Rue des Longs Reages, 28230 Épernon, France

Received: 30 September 2016 / Accepted: 05 December 2016 / Published online: 28 December 2016
© The Author(s) 2016. This article is published with open access.

1 Introduction

This fact sheet covers cement products whose ability to protect metal elements (reinforcements, inserts) from corrosion remains to be tested. We are going outside of conventional techniques, because no sufficient information is available to determine the passivation of submerged metallic elements in such conditions. Products may include metals whose behaviour in traditional concrete is not fully understood, or regular steel in cement matrices with a particular chemistry (low pH concrete, etc.). It is therefore important to directly assess corrosion risk without considering an initiation phase. The product is therefore considered in its initial state, unmodified by any possible carbonation or by the penetration of chlorides. For corrosion risks caused by carbonation or chloride ion penetration, please refer to those specific pathology sheets.

2 Consequences

- Reduction of reinforcement cross section.
- Cracking, spalling of the concrete cover.
- Loss of bond between the concrete and the reinforcements.

- Loss of load-bearing capacity of the reinforced structure (in extreme cases).

3 Physiochemical mechanisms

The corrosion of reinforcements is caused by a chemical reaction between the metal conductor and its aqueous environment. The main mechanisms involved (Figure 1) are described below.

- Corrosion occurs in the simultaneous presence of an oxidation reaction of the metal (anode) and a reduction reaction of oxygen (cathode).
- The rate of the electrochemical reactions taking place where the reinforcement and the concrete meet increases along with water content and decreases beyond a certain value due to falling oxygen diffusion.
- Redox reactions are followed by secondary reactions that form corrosion products (oxides and oxyhydroxides) on the surface of the metal.
- The nature of the environment surrounding the reinforcements (pH, temperature, resistance of the concrete's interstitial solution, chloride content, oxygen content, aggressive or inhibiting agent content,

* Corresponding author: Bruno Huet, LafargeHolcim R&D, 95 rue du Montmurier, 38291 Saint-Quentin-Fallavier Cedex, France, bruno.m.huet@lafargeholcim.com

etc.) changes the local thermodynamic equilibria and kinetics of redox reactions.

- Corrosion products are more or less stable and may in some cases continue to be formed until the reinforcement has corroded completely.
- In the case of steel, the corrosion products of iron that form on the steel's surface expand. This expansion creates internal stresses that promote the formation of cracks in the concrete surrounding the reinforcements.
- Cracks that reach the surface of the concrete significantly accelerate the diffusion of oxygen and water.

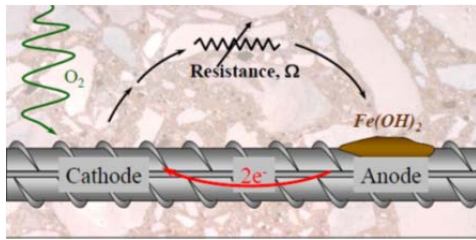


Figure 1. The basic mechanisms of steel corrosion in concrete.

4 Main models

- There is no agreed upon model (as of 2015) for predicting the corrosion of reinforcements.
- For example, the CORDOBA model [1] includes the transport of water and oxygen, the oxidation of steel, and mechanical factors.

5 Influential parameters

Material parameters:

- The concrete's ability to maintain an elevated pH in its interstitial solution over time, which keeps the metal in a stable state with a protective surface layer (the "passive" film).
- The concrete's microstructure (permeability and diffusivity) controls the ingress of water, oxygen, and other components that may increase corrosion rate.
- The type of metal.

Environment parameters:

- Relative humidity, rain, wind, sun exposure, temperature, and more generally the surrounding environment create fluctuations in the relative humidity and water content at the metal/concrete interface.
- The concentration of oxygen and other elements such as chlorides can increase corrosion rate (this is also true of the interstitial solution's conductivity).

6 Testing method stages

The testing method's key steps include:

- Preparing the electrodes (initial state of corrosion, cleanliness, attention paid to the electric connections, proper cover distances).
- Adjusting the environment's relative humidity and oxygen concentration (near to normal atmospheric oxygen concentration).
- Creation of a gaseous or liquid medium that represents the environment (anion content, i.e. chlorides, sulphates, etc.).

The quantities of interest may include:

- indicators such as the reinforcement corrosion potential [2] and concrete resistivity [3],
- polarisation resistance, which allows for the calculation of instantaneous corrosion rates [4],
- surface analyses to describe the homogeneity of the corrosion of the reinforcements submerged in the concrete at the end of the test.

Each of these quantities requires specific calibrated thresholds so as to assess the service life of reinforced structures.

7 Standard testing methods

Tests generally consist of taking electrochemical measurements of reinforced concrete as function of the ageing duration in their environment. These methods are fast (i.e. only a few minutes long). Therefore, the duration of the test is determined by the chosen ageing duration.

Additionally, submerged metallic elements may be extracted from the cement material after a certain period of time has passed for observation or analysis to verify the absence of corrosion products (experimenters often talk about sample "autopsies" in this instance).

Name	Environment	Laboratory or field conditions	Quantity of interest	Comments
NF EN 480-14 [5]	20 ± 2 °C, saturated calcium hydroxide solution	Laboratory	Maximum current density ($\mu\text{A}/\text{cm}^2$) after applying constant potential and visually inspection of the reinforcement at the end of the test	The sample containing the additive is compared with a control sample without the additive in order to assess the additive's effect on the corrosion process.
ASTM C876 [6]	Natural atmospheric environment	Laboratory conditions or field conditions	Corrosion potential Measure the potential difference between the reinforcement and the reference electrode placed in contact with the concrete's surface	Test requires a specialist intervention or supplementary data (chloride content, carbonation depth, etc.) to reach conclusions about service life of structures. There is work disproving this method for slag concrete
RILEM TC-154 EMC[3]	Measured in an atmospheric environment	Laboratory conditions or field conditions	Concrete resistivity Different principles play into these recommendations: 4-point method, method equivalent to ASTM C876 and other studies	Concrete resistivity measurements are generally correlated with chloride and water content. Information about reinforcement corrosion should be obtained using other methods.
CERIB Protocol [7]	Reproduction of the environment (humidity, drying, carbonation and/or chlorides, etc.) The reinforcement, the working electrode, and the reference electrode are submerged in the concrete	Laboratory	Corrosion potential and polarisation resistance	Comparative tests with a standardised control concrete are recommended.

8 Performance assessment

Assessment method:

- "comparative" assessment: the quantity of interest is measured for the candidate concrete, then compared to the values obtained from a standardised reference product using the same testing method.
- "absolute" assessment: currently, there is no absolute threshold value that has been defined in a sufficiently robust manner, some documents (ASTM C876 [6], RILEM TC-154 EMC [2-4]) list thresholds that are not agreed upon for all binders.

sion rate measurement of steel reinforcement in concrete by means of the polarization resistance method, Mater Struct (2004) 37: 623-643. <https://doi.org/10.1007/BF02483292>

- [5] NF EN 480-14:2006. Adjuvants pour béton, mortier et coulis - Méthodes d'essais - Partie 14 : détermination de l'effet sur la tendance à la corrosion de l'acier pour armature au moyen d'un essai électrochimique potentiostatique., 2006.
- [6] ASTM C 876:2009. Standard Test Method for Half-Cell Potentials of Uncoated Reinforcing Steel in Concrete., 2009.
- [7] J. MAI-NHU, Corrosion des armatures du béton : couplage carbonatation/chlorures en présence de cycles hydriques Université Toulouse III - Paul Sabatier, 2013.

References

- [1] A. Millard, V. L'Hostis, Modelling the effects of steel corrosion in concrete, induced by carbon dioxide penetration, Eur J Env Civil Eng, (2012) 16: 375-391. <https://doi.org/10.1080/19648189.2012.667976>
- [2] B. Elsener, C. Andrade, J. Gulikers, R. Polder, M. Raupach, Half-cell potential measurements - Potential mapping on reinforced concrete structures, Mater Struct (2003) 36: 461-471. <https://doi.org/10.1007/BF02481526>
- [3] R. Polder, C. Andrade, B. Elsener, O. Vennesland, J. Gulikers, R. Weidert, M. Raupach, Rilem TC 154-EMC: Electrochemical techniques for measuring metallic corrosion - Test methods for on site measurement of resistivity of concrete, Mater Struct (2000) 33: 603-611. <https://doi.org/10.1007/BF02480599>
- [4] C. Andrade, C. Alonso, J. Gulikers, R. Polder, R. Cigna, O. Vennesland, M. Salta, A. Raharinaivo, B. Elsener, Test methods for on-site corro-

Supplementary material

Durability performance assessment of non-standard cementitious materials for buildings: a general method applied to the French context

Fact sheet 4 - Risk of concrete damage by internal freezing

Pierre Pimienta^a, Blandine Albert^b, Bruno Huet^{b*}, Michael Dierkens^c, Philippe Francisco^d,
Patrick Rougeau^d

^a Université Paris-Est, CSTB, 84 avenue Jean Jaurès Champs-sur-Marne, 77447 Marne-la-Vallée Cedex 2, France

^b LafargeHolcim R&D, 95 rue du Montmurier, 38291 Saint-Quentin-Fallavier Cedex, France

^c CEREMA, 25, avenue François Mitterrand - CS 92 803, 69674 Bron Cedex, France

^d CERIB, 1 Rue des Longs Reages, 28230 Épernon, France

Received: 30 September 2016 / Accepted: 05 December 2016 / Published online: 28 December 2016
© The Author(s) 2016. This article is published with open access.

1 Introduction

This type of degradation affects hardened concretes that are subjected to "severe" or "moderate" freezing conditions. For France, the geographic zones concerned are defined in the booklet FD P 18-326-2004 [1]. Generally speaking, the definition used comes from the 2003 LCPC Recommendations guide [2]: the areas of severe freezing reach temperatures below -10°C more than ten days out of the year and the areas of moderate freezing reach a temperature below -5°C more than two days per year. This fact sheet only addresses degradation linked to simple freezing, called "internal freezing", i.e. freezing in the absence of de-icing salts (see the dedicated sheet on concrete scaling during freeze/thaw cycles).

2 Consequences

- Swelling of the concrete.
- Internal micro-cracking.
- Decrease of mechanical performance (bulk modulus, compressive strength).

- Aggregate are dislodged due to loss of cohesion with the hydrated cement paste leading to the destruction of pieces of concrete in extreme cases.

3 Physiochemical mechanisms

When a cementitious material, partially saturated with interstitial solution, is subjected to freezing and thawing temperature cycles in the presence of humidity, internal damage by freezing may occur. The risk of degradation is related to fluid pressure after some of the water contained in the porous network freezes. There are several theories that may describe the phenomenon, but none gives a perfectly satisfying explanation for all experimental evidence. The most commonly used is explained below.

Powers' theory of hydraulic pressure [3]:

When the temperature falls, the water contained in the porous network freezes progressively based on capillary diameter (first in the largest pores, then in the smaller ones). As it freezes, the volume of this water increases, creating hydraulic pressure in the water that remains in a liquid state (see Figure on the left below). This increase in liquid pressure creates stresses in the cement paste, which may lead to its

* Corresponding author: Bruno Huet, LafargeHolcim R&D, 95 rue du Montmurier, 38291 Saint-Quentin-Fallavier Cedex, France, bruno.m.huet@lafargeholcim.com

cracking if the stresses generated exceed the material tensile strength.

It has been observed in poured concrete that the presence of dispersed air voids in the paste improved resistance to freezing/thawing cycles. Air content seems to help reduce hydraulic pressure by facilitating the flow of unfrozen solution. By applying Darcy's law to the flowing fluid, Powers [3] was able to determine the ideal distribution of air voids in order to limit the generated stresses. That is why concrete is often formulated with an air-trapping agent that stabilises the air that is incorporated during mixing. The distribution of air voids is characterised by a spacing factor ($\bar{L}$), which is the average half distance between voids in the paste (see Figure 1b) and the testing method in section **Error! Reference source not found.**). Taking a "critical" threshold into account helps to ensure proper resistance to freezing/thawing cycles. It should be noted that concrete can still be quite resistant without this network of voids in certain cases (for example, UHPC, HPC with a W/C ratio below 0.32). On the other hand, staying below this threshold does not, in and of itself, guarantee that the concrete will behave well when frozen if it has an unconventional composition, e.g. an aggregate that is sensitive to freezing, or a paste with insufficient tensile strength, etc.

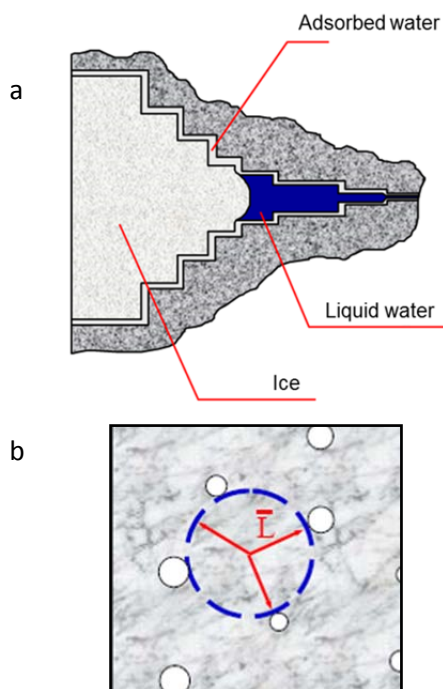


Figure 1. Ice formation in a pore as a function of radius (a) [13] and spacing factor ($\bar{L}$) (b).

4 Main models

There is no agreed-upon predictive model (as of 2015). Q. Zeng's thesis [4] offers a bibliographical synthesis on the topic.

5 Influential parameters

Material parameters:

- Concrete composition:
 - type and frost-sensitivity of the aggregate; the concrete must be formulated with aggregate or other inclusions that are not susceptible to frost),
 - presence or absence of a network of air voids, and, if they are present, the characteristics of this network,
 - structure of the porous network of the cement paste described by its pore size distribution.
- Age of the product – Strong impact on concretes that experience freezing before 28 days curing.
 - Concrete may be susceptible to frost starting with the first few exposure cycles. The age of the material can change its susceptibility to frost: significant damage may be observed in case of early exposure, for example.
- Methods of concrete placing: poor compacity if there is insufficient vibration, bad air void network because of pumping conditions, drop height, excessive vibration,...
- Mechanical tensile strength (generally indirectly assessed by measuring compressive strength).
- Water saturation of the product: the higher it is, the more susceptible to frost is the material.

Environment parameters:

- Cycle type (thermal and hydrological conditions).
 - Based on the type of cycle (amplitude, frequency) and thermal diffusion, the product may be frozen to its core.
- Degree of inclination of the structure (horizontal, drained surface, surfaces).

6 Testing method stages

- Compaction methods, which strongly influence the structure of the porous network, especially when the concrete contains air voids.
- Age of the concrete.
- Curing duration and conditions (temperature, generally stored in water): a 28-day cure is common for cement materials. The methods can be adapted based on the specificities of the material and its application, especially the amount of time it takes for the properties to stabilise. In all cases, this duration must be compatible with the age of the concrete when it is first exposed to freezing temperatures.
- Creation of measurement plots to track deformation (if applicable).
 - according to the reference testing methods.
- When measurements are taken:

- sample thawing conditions before measurement.
- measurements of the resonance frequency and the relative expansion.

The quantities of interest may be:

- Spacing factor (if necessary).
- Expansion (non-destructive measurement), changes in the resonance frequency or in the speed of sound (also non-destructive measurements).
- Loss of mass (non-destructive measurement).
- Residual mechanical properties (destructive measurement).

7 Standard testing methods

Apart from the air void network characterisation tests, the other performance tests generally involve exposing concrete samples to freezing/thawing cycles, then detecting any degradation after a certain number of cycles. There are other specific standards that can be applied to particular concrete industrial products (for example, standard NF P 98-052 2002 [5] for monoblock window supports).

It should be noted that there is a specific test for freeze/thaw cycle resistance for aggregate, which may be applied to a new product of this kind.

Table 1. Tests listed in current provisions valid in the place of use for conventional concrete:

Name	Cure	Thermal cycle	Duration	Comment
ASTM C 457M :2012 [6]	7 days under water.	-	total time: about 1 week, including 2h of counting.	Measurement: spacing factor.
NF EN 480-11 :2006 [7]	7 days under water.	-	total time: about 1 week	Measurement: spacing factor by image analysis. Used to characterise additive effectiveness.
NF P 18 424 [8]	28 days under water. T=20°C±2	300 cycles [-18°C ; + 9 °C] 4 cycles / 24 hours. Freezing in water and thawing in water	3.5 months	Concrete performance test
NF P 18 425 [9]	28 days under water. T=20°C±2	300 cycles [-18°C ; + 9 °C] 4 cycles / 24 hours. Freezing in air and thawing in water	3.5 months	Concrete performance test
PD CEN/TR 15177 :2006 [10]	In a closed system for 6 days then under water for 21 days T=20°C±2	56 cycles [-20°C ; + 20°C] 2 cycles / 24 hours. Freezing in air and thawing in water	56 days	Concrete performance test
NF EN 1367-1 :2007 [11]	1) Washing, 2) drying at 110°C±5.3) imbibition under water at 20°C±5 for 24±1 hours	10 cycles [-17.5°C ; + 20°C] 1 cycle/24 hours. Under water	≈ 13 days	Aggregate test

8 Performance assessment

Assessment method:

- "absolute" binary assessment: if the measured quantity of interest of frost-resistant material meets the corresponding critical threshold values, the product is considered as performing and conform.

For the standards NF P 18-424 [8], NF P 18-425 [9], and ASTM C 457M [6], mentioned in the table above, the conformity interpretation thresholds are defined in the 2003 LCPC Recommendations guide [2].

References

- [1] FD P18-326:2004. Béton - Zones de gel en France., 2004.
- [2] L.-L.C.D.P.E. CHAUSSEES, Recommandations pour la durabilité des bétons durcis soumis au gel, 2003.

- [3] T.C. Powers, Void Spacing as a Basis for Producing Air-Entraining Concrete, Highway Research Board, 29 (1949) 184–211.
- [4] Q. Zeng, Poromechanical behavior of cement-based materials subjected to freeze-thaw actions with salts modeling and experiments., Laboratoire Navier, UNIVERSITÉ PARIS–EST, 2011, pp. 298.
- [5] NF P98-052:2002. Produits préfabriqués en béton - Appuis de fenêtre préfabriqués en béton., 2002.
- [6] ASTM C 457M:2012. Standard Test Method for Microscopical Determination of Parameters of the Air-Void System in Hardened Concrete., 2012.
- [7] NF EN 480-11:2006. Adjuvants pour béton, mortier et coulis - Méthodes d'essai - Partie 11 : détermination des caractéristiques des vides d'air dans le béton durci., 2006.
- [8] NF P18-424:2008. Bétons - Essai de gel sur béton durci - Gel dans l'eau - Dégel dans l'eau., 2008.
- [9] NF P18-425:2008. Bétons - Essai de gel sur béton durci - Gel dans l'air - Dégel dans l'eau., 2008.
- [10] PD CEN/TR 15177:2006. Testing the freeze-thaw resistance of concrete. Internal structural damage., 2006.
- [11] NF EN 1367-1:2007. Essais de détermination des propriétés thermiques et de l'altérabilité des granulats - Partie 1 : détermination de la résistance au gel-dégel., 2007.

Fact sheet 5

Risk of concrete scaling during freeze/thaw cycles in presence of de-icing salt

1. Introduction

There is a risk of scaling degradation for concrete that is subjected to freeze/thaw cycles in the presence of de-icing salts (NaCl, CaCl₂). However, scaling is also sometimes observed in concrete that is subjected to freezing and thawing without the presence of de-icing salts as well as in concrete exposed to salt (seawater) without exposure to freezing/thawing cycles. These two instances are not discussed in this sheet.

In order to prevent scaling damage, it is necessary to pre-emptively protect against the problems related to simple freezing (see fact sheet on "concrete damage by internal freezing"). This sheet discusses instances salting that are considered as "frequent" (between 10 and 30 days per year) and "very frequent" (more than 30 days per year).

2. Consequences

- Concrete scales from the surface to the core of concrete with significant mass loss.
- Cracking or removal of aggregate that is not considered susceptible to freezing.

3. Physiochemical mechanisms

Given that all scaling pathologies cannot be explained in the same way and are the subject of constant research, the scientific and technical communities are not able to agree upon a single model that explains this phenomenon, though they are able to rank the different influential parameters. A summary of the different mechanisms identified in the literature is given in [8] and [9].

Nevertheless, the mechanisms below are frequently identified:

- the core of the concrete, which contains fewer chloride ions in solution, freezes more easily than the surface. The result is an expansion of the core when it is frozen, along with shrinkage on the surface: the resulting differential stresses create a tensile break within the paste,
- the freezing temperature of water is a direct function of pore diameter and of the concentration of dissolved salts.

As it is suggested in [9], the severity of the damage caused by the combined action of freeze-thaw cycles and de-icing salts is mainly due to the surface's greater susceptibility to frost (higher volume of paste and therefore, greater porosity) and to winter conditions that exacerbate defects by maintaining saturation, by subjecting the surface to thermal shocks, and by creating saline concentration gradients (osmosis, freezing layer by layer).

4. Main models

There is no agreed-upon predictive model (as of 2015). However, several models have been published, such as Valenza and Scherer's model [1, 2], for example, to explain concrete behavior in laboratory tests.

5. Influential parameters

"Material" parameters:

- product composition: the paste tensile strength, the aggregate susceptibility to frost),
- transport properties of liquid water and chlorides,
- structure of the porous network:
 - o entrained air, trapped air (quantity and spatial distribution).
 - o pore size and distribution.

"Environment" parameters:

- cycle type (thermal and hydrological conditions),
- degree of inclination of the structure (horizontal surface, drainage, inclined surface),
- presence of salts (type, concentration, frequency of application).

6. Steps of the test protocol to be studied:

Tests generally involve exposing to freeze/thaw cycles samples that have one surface in contact with a given volume of brine.

- Test sample preparation methods. Compaction methods have a strong influence on the structure of the porous network. The test surface must be undamaged and may be influenced by the mould type and preparation (choice of wax).

- Curing length and conditions:
 - o age of the concrete. Strong impact on concretes that experience freezing before 28 days curing.
 - o curing in liquid water: impact of temperature only.
 - o curing in air: impact of CO_{2(g)} content, temperature and relative humidity on concrete surface carbonation and hydration.
- Observance of freezing/thawing cycles. Adjustment of the climatic chamber, placement of temperature probes, brine depth.
- Brine composition. Pessimism effect of the chloride concentration on the scaled mass. Impact of the brine (concentration, homogeneity, and depth) on thermal regulation.
- Assessment of real exposed surface.

The quantity of interest is the cumulative mass loss of scales expressed in gram per square meter. It is influenced by the method of scales collection and by the effective test surface area.

7. Standard testing methods

Name	Cure	Thermal cycle	Duration	Comment
XP P18-420:2012 [3]	150x150x150 mm Cube. 14 days in water. Cubes sawed between 7 and 14 days. Up to 28 days in air (20°C, 65% RH). After 28 days, 3-day resaturation with 3 mm of tap water. After 31 days, the water is replaced with a 3% NaCl salt solution for the test.	-20 + 20°C	3 months	In France, testing is done on the formed surface. Thresholds are available [4].
DD EN 12390-9:2006 [5], Slab test	150x150x150 mm Cube. 7 days in water at 20°C, then up to 25 days in air (20°C, 65% RH, 45 g/m ² /h and 300-1100 ppmv CO ₂) The block is sawed after 21 days, configured on the 25th day After 28 days, 3-day resaturation with 3 mm of tap water. After 31 days, the water is replaced with a 3% NaCl saline solution when the test starts.	-20 / +20°C	3.3 months	Test surface: sawed face.
EN 12390-9:2006 [5], Cube test	100x100x100 mm Cubes. 7 days in water at 20°C, then up to 27 days in air (20°C, 65% RH, 45 g/m ² /h and 300-1100 ppmv CO ₂) After 27 days, the cubes are placed in containers that are filled with a 3% NaCl solution (complete immersion) On the 28th day, the test begins.	-15 / +20°C	3 months	
EN 12390-9:2006 [5], CF/CDF Test	150x150x150 mm Cubes and separation plate. 7 days in water at 20°C, then up to 28 days in air (20°C, 65% RH, 45 g/m ² /h and 300-1100 ppmv CO ₂) Resaturation on the 28th day through capillary absorption and beginning of the tests. Freezing medium: - CF Test: demineralized water. - CDF Test: 3% NaCl solution.	-20 / +20°C	CDF Test: 2 months CF Test: 3 months	

8. Performance assessment

To ensure the freeze-thaw performance of a composition, a product should meet the performance requirements of both internal frost resistance and scaling resistance.

For aspects related to simple freezing, the fact sheet on internal freezing may be consulted. For simple freezing, the assessment method is “absolute” binary. The assessment method for scaling is also “absolute” binary.

For standard XP P18-420:2012 [3] mentioned in the previous table, the threshold values from the recommendations for the durability of concrete subjected to freezing may be used [4].

9. References

- [1] J.J. Valenza, II, G.W. Scherer, A review of salt scaling: I. Phenomenology, Cement and Concrete Research, 37 (2007) 1007-1021.
- [2] J.J. Valenza, II, G.W. Scherer, A review of salt scaling: II. Mechanisms, Cement and Concrete Research, 37 (2007) 1022-1034.
- [3] XP P18-420:2012. Béton - Essai d'écaillage des surfaces de béton durci exposées au gel en présence d'une solution saline., 2012.
- [4] Recommandations pour la durabilité des bétons durcis soumis au gel : Guide technique, in: L.C.D.P.E.C.-. LCPC (Ed.) Techniques et méthodes des laboratoires des ponts et chaussées, 2003, pp. 167.
- [5] DD CEN/TS 12390-9:2006. Testing hardened concrete. Freeze-thaw resistance. Scaling., 2006.
- [6] SS 137244:2005. Concrete testing - Hardened concrete - Scaling at freezing., 2005.
- [7] NF EN 13369:2013. Règles communes pour les produits préfabriqués en béton., 2013.
- [8] S. Bouteille, Outils de caractérisation et analyse du comportement des matériaux cimentaires soumis à des cycles de gel-dégel en présence de sels., Université Paris-Est, 2013, pp. 303.
- [9] J.-P. Ollivier, A. Vichot, La durabilité des bétons, ATILH, 2008.

Fact sheet 6

Risk of degradation from an External Sulphate Attack (ESA)

1. Introduction

This degradation risk affects concrete that is exposed to an environment rich in soluble sulphates.

There are several types of external sulphate reaction. The first kind of reaction leads to the formation of secondary expansive ettringite. The second kind of reaction, which is quite uncommon, leads to the formation of thaumasite. There can also be purely physical degradation due to salt crystallisation. Only the first reaction will be discussed in this document.

2. Consequences

This degradation can create a wide and varied range of disruptions:

- swelling.
- cracking on several scales: scaling, surface flaking, or blister (craters with localised scaling).
- in the worst case, concrete may lose cohesion.

Many of the disorders affect parts of structures that are barely or not at all accessible (foundations, pipelines, etc.), which probably leads us to underestimate their occurrence.

3. Physiochemical mechanisms

The rate at which these problems appear and grow as well as where their locations are highly variable. Such problems often remain relatively superficial (a few centimetres in depth), but they can affect a large area of the concrete protective layer covering the metallic reinforcements. Stopping reactions or even repairing the reacted material remain a challenge once degradation has started.

The mechanisms associated with ESA have not yet been established with certainty, but with our current level of understanding, we can propose the following steps for Portland cement-based concretes.

1. In the first days of the material's hydration, calcium monosulfoaluminate macro-crystals and crystallites form within the C-S-H hydrates from a combination of C_3A and the sulphates present in the binder.
2. Sulphate ions from the environments penetrate the material following two modes of transport: by diffusion when the material is saturated with water, or by advection when the material is under a hydraulic pressure gradient or during wetting/drying cycles. Surface cracking of the concrete also accelerates ion ingress.
3. These sulphate ions react with the monosulfoaluminate crystallites, which slowly transform into ettringite crystallites (calcium trisulfoaluminate). Depending on the supersaturation levels reached on a localised level and on confinement conditions, the formation of ettringite creates stresses that can lead to paste damage and a loss of bond between the paste and the aggregate. The calcium monosulfoaluminate macro-crystals also transform into ettringite, but it seems they do not cause such problems. Over time, some ettringite crystallites dissolve and large ettringite crystals form in the interfacial transition zone between the paste/the aggregate opened up by the previous step, increasing the disorder. At high sulphate concentrations, the formation of gypsum has also been observed.

The presence of hydraulic or pozzolan mineral additions in sufficient quantities often helps to reduce these disorders. Though the reason why is still poorly understood, calcareous fillers seem to accelerate degradation. The fineness of cement, the size of the concrete structure, and its geometry also seem to influence the rate of the swelling. Even if a material is resistant to sea water, that does not mean that it will also be resistant to sulphates.

Sea water and chlorinated de-icing salts contain soluble sulphates, but there is a competition between the fixation of sulphates and that of chlorides in the aluminate phases. The soluble sulphates can be the result of the oxidation of iron sulphides.

4. Main prediction models

There is no agreed-upon predictive model (as of 2015).

5. Influential parameters

"Material" parameters:

- Cement mineralogy: C_3A concentrations for Portland cements (*the concentration of C_4AF can also play a role*), concentration of C_3S and alkalis.

- Type and concentration of the main hydraulic or pozzolan components in the cement or mineral additions in the concrete.
- Concrete's water/binder ratio and other factors may affect the material's final compacity (the compacity of the granular skeleton, the concrete placing, its curing, etc.)
- Size and geometry of the test samples.

For more details on the influential parameters for traditional concretes, please refer to the GRANDUBE work group's bibliographical review "Endogenic reactions" [9].

"Environment" parameters:

- The sulphate ion concentration at the concrete's surface as well as the type of associated cation (Ca^{2+} , Na^+ , Mg^{2+}).
 - Degradation in the presence of magnesium sulphate is generally more pronounced for Portland cement-based materials (C-S-H degrades into "M-S-H", which has no binding property).
- The rate of sulphate ion renewal at the concrete's surface.
- The frequency of wetting/drying cycles at the concrete's surface, when these cycles have a significant impact on the water saturation degree of the first few centimetres of the concrete surface.
- The temperature.

6. Testing method stages

Tests can be divided into qualitative binder assessment tests, generally carried out on mortars (test samples are 2x2x16 or smaller, thin plates, etc.), and concrete performance tests, carried out on prisms, cylinders, or cores. The smaller the sample, the faster the test.

Tests generally follow the same outline:

- moist curing of the test sample.
- immersion in a sulphate solution at 20-23°C depending on the country.

These tests are often long (several months for mortar, sometimes several years for concrete). To accelerate the degradation process, some tests include:

- cycles of drying and immersion of test samples.
- a drying phase followed by a single saturation in a vacuum using the sulphate solution at the beginning of the test.

Most tests use Na_2SO_4 solutions, with concentrations that range from 16-33 g of SO_4 /l. Some tests use a less concentrated solution, which makes the test longer if no other means of accelerating reactions is used. Magnesium sulphate is more aggressive. Gypsum is markedly less soluble and leads to longer test durations. The salt to be used may be chosen based on the environmental conditions planned for the material to be tested.

For some tests, the pH of the sulphate solution is regulated, which speeds up the test and makes it more representative of mediums with constant compositions. In many tests, in order to maintain the most constant sulphate levels possible throughout the test (since the material consumes sulphate), the sulphate solution is renewed regularly (often when measurements are taken). A large solution / material volume ratio is also recommended.

The measured quantities of interest are:

- the longitudinal deformation and the mass of test samples.
- but also sometimes the mass of scales produced, the density, strength, dynamic elasticity, or the flux of leached materials.

7. Standard testing methods

Today, there is a wide range of possible tests, but very few have led to any kind of consensus.

Tests listed in current rules for on-site use with conventional concrete:

Name	Curing	Sample	Immersion conditions	Test duration	Quantity	Comment
CSA A3004-C8 - Procedure A [1] and ASTM C1012 :2013 [3]	Under water until $R_c > 20\text{MPa}$	Mortar strips of 2.5*2.5*28.5 cm	$[\text{SO}_4^{2-}] = 2.8 \text{ g/l}$ (Na_2SO_4 solution) at 20°C	12 or 24 months	expansion	
SIA 262/1:2013 [4] appendix D	28 day under water.	28mm diameter 150mm concrete core	4 cycles of 2 days of drying and 5 days in a 33 g SO_4^{2-} /l	56 days	expansion and mass	Concrete performance test

P. Pimienta, B. Albert, B. Huet, M. Dierkens, P. Francisco, P. Rougeau, Durability performance assessment of non-standard cementitious materials for buildings: a general method applied to the French context, RILEM Technical Letters (2016) 1: 102 – 108, DOI: <http://dx.doi.org/10.21809/rilemtechlett.2016.17>
Supplementary Materials.

			solution of Na ₂ SO ₄			
NF P18-837 [5]	28 day under water.	Mortar strips of 2*2*16 cm	[SO ₄ ²⁻] = 19.5 g/l (MgSO ₄ solution) at 20°C	56 weeks	expansion	

Alternative testing methods:

Cur Recommendation 48 [6]	28 day under water.	Mortar strips of 2*2*16 cm	[SO ₄ ²⁻] = 16 g/l (Na ₂ SO ₄ solution) at 20°C	56 weeks	expansion	
Wittenkind Test [7]	demoulding at 2 days, then 14 days in limewater	Mortar strips of 1*4*16 cm	[SO ₄ ²⁻] = 29.5 g/l (Na ₂ SO ₄ solution) at 20°C and 5°C	>= 7 months	expansion and dynamic elasticity modulus	Control sample in limewater recommended

Other methods may be found in the state of the art section of document PD CEN/TR 15697-2008 [8].

8. Performance assessment

Some of these tests have thresholds for an "absolute" assessment. The reader is invited to consult the testing methods or the associated document booklets to find these thresholds. These thresholds are specific to each test; they can by no means be used for other tests before they are approved through adequate study.

9. References

- [1] CAN/CSA-A3000-13 - Cementitious materials compendium, 2013, pp. 282.
- [2] ASTM C 452/C 452M:2010. Standard Test Method for Potential Expansion of Portland-Cement Mortars Exposed to Sulfate., 2010.
- [3] ASTM C 1012/C 1012M:2013. Standard Test Method for Length Change of Hydraulic-Cement Mortars Exposed to a Sulfate Solution., 2013.
- [4] SIA 262/1:2013 Construction en béton - Spécifications complémentaires, 2013.
- [5] NF P 18-837:1993. Produits spéciaux destinés aux constructions en béton hydraulique - Produits de calage et/ou scellement à base de liants hydrauliques - Essai de tenue à l'eau de mer et/ou à l'eau à haute teneur en sulfates., 1993.
- [6] CUR-aanbevelingen 048:2010 Procedures, criteria en beproevingsmethoden voor de toetsing van de geschiktheid van nieuwe cementen voor toepassing in beton en voor de gelijkwaardige prestatie van beton met vulstoffen, 2010.
- [7] Wittekindt, Sulphate-resistant cements and their testing, Zement Kalk Gyps, (1960) 565 - 572.
- [8] PD CEN/TR 15697:2008. Ciment. Essais de performances relatifs à la résistance aux sulfates. État de l'art - Ciment. Performance testing for sulfate resistance. State of the art report., 2008.
- [9] GranDuBé, (2007) Grandeurs associées à la Durabilité des Bétons, sous la direction de G. Arliguie et H. Hornain, Presses de l'Ecole Nationale des Ponts et Chaussées, 2007.

Fact sheet 7

Risk of degradation by an Internal Sulphate Attack (ISA)

1. Introduction

The risk of Delayed Ettringite Formation (DEF) affects concretes that have been heated over 65°C for several hours or several days after installation and that are made up of a cement matrix whose physio-chemical characteristics favour DEF. Only DEF, a specific form of Internal Sulphate attack (ISA), is addressed here. Damage may occur if these concretes are then exposed to a very humid environment.

This scenario may affect concrete structures that generate great heat during binder hydration that is only partially evacuated to the exterior (large structures, compositions with high hydration heat cements, use of insulating formwork), or those that are subjected to high temperatures at a young age (concrete poured during hot weather, excessive thermal treatment). The degradation is linked to late formation (over several years) in humid environment of large deposits of very expansive secondary ettringite that can ruin the structure.

N.B.: For Portland cement-based concrete, the basic parameters are water, the maximum temperature reached, how long this temperature is maintained, the sulphate and aluminate content of the cement and the alkali content of the concrete. It has been shown at the laboratory scale that if temperatures exceed 65°C and if the other basic parameters are present, DEF may develop. Even for materials that do not experience ettringite formation, excessive heating at a young age should be avoided in order to prevent thermal stress due to self-restraint and the appearance of thermal cracks when the concrete cools down.

2. Consequences

- Large and deep cracks in the core of concrete.
- Very significant loss of mechanical properties.
- Increased risks of reinforcement corrosion and failure due to cracking of the concrete cover.

3. Physiochemical mechanisms

The conditions that lead to harmful swelling due to an ISA are not yet fully understood. This phenomenon was only recently identified as opposed other known concrete pathologies (in the 1980s) and the link between laboratory tests and behaviour in the field is tenuous. All mechanisms are not yet fully understood, but the current research work suggests that the degradation is the result of a combination of the following mechanisms:

- if the temperature of the concrete is over 65°C during the days after its hydration begins, primary ettringite, which forms normally, does not form or is unstable and disappears. Sulphate and aluminate ions that are not used to make primary ettringite form calcium monosulfoaluminate microcrystals that are dispersed throughout the C-S-H; sulphates also adsorb onto the C-S-H surface whereas aluminium is integrated into the C-S-H structure [5].
- A pessimum effect linked to temperature/heating duration appeared after some laboratory tests [6] [7]. This means that there is no one threshold temperature, but rather a specific threshold temperature for each case study. This is for example the reason why short heat treatments used in the precast concrete industry are permitted by the ISA recommendations [3], despite the use of temperatures above 65°C.
- if, over the months and years following placing, the material is in frequent contact with free water (stagnant water, immersion, etc.), the calcium monosulfoaluminate microcrystals will react with the sulphate and aluminate ions freed by the C-S-H to form massive and expansive secondary ettringite. In this instance, the cement paste is subject to generalised expansion that leads to cracking of concrete. This reaction is generally quite slow and the first signs of structural degradation often do not appear for at least 10 years. Wetting/drying cycles seem to accelerate the formation of secondary ettringite.

4. Main models

There are existing models to predict the temperature rise in concrete structures, allowing for preventive measures to be taken. The most complete model is the CESAR-LCPC model [1] developed by IFSTTAR; it returns 2D or 3D temperature maps of concrete pieces over time). The RGIB module [2] of this model allows resulting expansion due to an internal reaction (alkali-aggregate reaction and internal sulphate attack) to be estimated.

As a first approach, appendix IV of the LCPC Recommendations [3] may be used, which gives a formula for estimating the maximum temperature reached within a concrete element.

5. Influential parameters

"Material" parameters that contribute to temperature rise within concrete:

- dimensions of the concrete element,
- binder type and content within the concrete:
 - hydration heat of the cement,
 - the presence of one or several reactive additives (slag, fly ash, natural pozzolans, metakaolin, and silica fumes) in specific proportions can reduce the increase in temperature when the additives are used as clinker replacement,
- type of aggregate.

"Material" parameters that facilitate ISR in the case of high temperatures at a young age:

For materials that meet current concrete standards, the current parameters are given below:

- binders that are rich in aluminates, sulphates, and alkalis are the most susceptible to this phenomenon (nevertheless, using a CEM I SR cement is not enough to guarantee that no ISA will occur),
- the presence of one or several additives may, depending on the type used, promote the binding of sulphates in non-expansive forms (increase of the critical threshold temperature [3]).

"Environment" parameters that contribute to rising temperatures within the concrete:

- temperature of the concrete's constituents when they are mixed and the temperature of the concrete when it is placed,
- external temperature when the concrete is placed and in the days that follow,
- the presence of an insulating formwork,
- thermal treatments: maximum temperatures that are too high and periods of high temperature that are too long should be avoided [3].

"Environment" parameters that facilitate ISA in the case of high temperatures at a young age:

- frequent wetting/drying cycles or constant contact with free water.

6. Testing method stages

The link between laboratory tests and the reality in the field requires further study because this type of degradation was only identified recently and remains relatively rare. The laboratory test developed and published by IFSTTAR in 2007 is one example [4]. It involves proving whether the ISR phenomenon can develop for a given concrete composition and for a given thermal heating:

- Samples of concrete (with measuring inserts to track dimensional variation) are made, then quickly exposed to a heat treatment that is characterized by the speed of heating, the duration of the period of sustained heat, the maximum temperature, and the speed of cooling. There is no standard treatment suggested by the test. This treatment would need to reflect a real exposure scenario, whether known or estimated, as indicated in section 4.
- The samples are then subjected to wetting/drying cycles. This cycles help to accelerate the degradation mechanisms, shortening them by several weeks.
- The test samples are then stored in water. Weight and dimensional variation measurements are taken regularly for at least one year. Based on the observed trends, the total duration of the test may be between 12.5 and 15.5 months, including the initial treatment. A SEM (Scanning Electron Microscope) image analysis should be done at the end of the test to make sure that the degradation is in fact the result of expansive secondary ettringite formation.

The quantities of interest are:

- weight and dimensional variations of the test samples.
- the massive formation of ettringite in the material after testing, observed, for example, with the SEM.

7. Standard testing methods

For France, the test was developed by IFSTTAR and published in 2007.

Name	Initial treatment	Pre-conditioning	Measurements	Total test duration	Thresho Id	Comment
LCPC- ME66: 2007 [4]	Heat treatment representing the heat history of the concrete structure until it reaches ambient temperature.	2 cycles (of 7 days each) of drying (RH < 30% [38 ± 2]°C)/ wetting (RH = 100% [20 ± 2]°C) Then storage in water at [20 ± 2]°C.	Weight and dimensional variations every 7 days for 2 months, then every 15 days for 4 months, then every month	Between 12.5 and 15.5 months including the initial treatment	Criteria according to [4]	This qualitative test is generally seen to be conservative. The standard deviation is quite high.

8. Performance assessment

Assessment method:

- "absolute" assessment: the quantity of interest should remain below the thresholds recommended in the LCPC ISR guide [3] and the LPC No. 66 [4] testing method.

9. References

- [1] P. Humbert, A. Dubouchet, G. Fezans, D. Remaud, CESAR-LCPC, un progiciel de calcul dédié au génie civil, Bulletin des Laboratoires des Ponts et Chaussées, Bulletin des Laboratoires des Ponts et Chaussées, (2005) 7-37.
- [2] N. Baghdadi, Modélisation du couplage chimico-mécanique d'un béton atteint d'une réaction sulfatique interne., ENPC, 2008, pp. 248.
- [3] LCPC, Recommandations pour la prévention des désordres dus à la réaction sulfatique interne - Guide technique., 2007.
- [4] LCPC, A. Pavoine, L. Divet, ME66. Réactivité d'un béton vis-à-vis d'une réaction sulfatique interne. Essai de performance., 2007.
- [5] Barbarulo, R. 2002. Comportement des matériaux cimentaires : actions des sulfates et de la température. Ph.D. thesis, Ecole Normale Supérieure de Cachan, Université Laval.
- [6] Barbarulo, R., Peycelon, H., Prené, S., & Marchand, J. 2005. Delayed ettringite formation symptoms on mortars induced by high temperature due to cement heat of hydration or late thermal cycle. Cement and Concrete Research, 35(1), 125 – 131
- [7] Brunetaud, X. 2005. Etude de l'influence de différents paramètres et de leurs interactions sur la cinétique et l'amplitude de la réaction sulfatique interne au béton. Ph.D. thesis, Laboratoire Central des Ponts et Chaussées et le laboratoire MSSMat.

Fact sheet 8

Risk of degradation by an Alkali-Silica Reaction (ASR)

1. Introduction

Alkali reactions are a range of reactions between certain soluble forms of silica or silicates and the alkali present in concrete in presence of water. This reaction creates an expansive gel that, in extreme cases, can destroy parts of the structures it affects. The general procedure for preventing this reaction is described in FD P 18464 [1].

2. Consequences

- Large and deep cracks in the affected concrete elements.
- Very significant loss of mechanical properties.
- Increased risk of steel corrosion due to concrete cracking and failure of reinforcement.

3. Physiochemical mechanisms

Current work highlights the importance of the mechanisms described below.

Solubility of certain unstable forms of silica or silicates in alkaline environment.

The FD P 18 542 [2] documentation booklet details how aggregate is classified into three categories: non-reactive (NR), potentially reactive (PR), and potentially reactive with pessimum effect (PRP). For this last category, the risk is only present when soluble silica content falls within certain "pessimal" critical value ranges.

This classification is done based on some or all of the following criteria:

- silica content
- petrographic analysis
- performance testing (screening test or long-term test).

Quantity of accessible alkalis.

Risk exists above ~3 kg of alkaline equivalents per cubic metre of concrete (taking K and Na into account). The alkalis that may contribute to these reactions are those present in the interstitial solution, which may come from any of the constituents (binder, mineral additive, admixture, aggregate, etc.).

Some environments, such as marine environments or those where de-icing salts are used are more aggressive because they enrich the concrete's interstitial solution with alkalis.

Presence of liquid water.

If, in the months and years after its placing, the material comes into frequent contact with free water (stagnant water, a immersed element, etc.), an expansive silico-calco-alkaline gel forms. In this instance, the cement paste is subject to generalised expansion that leads to cracking. This reaction is generally quite slow and the first signs of structural degradation often do not appear for at least 10 years.

4. Main models

The RGIB model [3], which is part of the César-LCPC calculation code [4] is an example of a model that describes the structural expansion associated with ASR.

5. Influential parameters

"Material" parameters:

- Quantity and stability of the aggregate silica in a basic medium: aggregate classification into NR, PR, or PRP.
- Total alkaline equivalents generated by all components that may be found in solution and may be available for reactions (total calculated using the instructions given in FD P 18 464 [1]).
- Amount of binder, which is generally the main source of alkalis.
- Mineral additives, depending on their nature and amount, which may reduce or even counteract this phenomenon. The most effective additives are low-calcium silico-aluminous fly ash, blast furnace slag, and metakaolin. s

"Environment" parameters:

- Wetting/drying frequent cycles or constant contact with free water.
- Ingress of alkalis from external sources (de-icing salts, marine environment).

6. Testing method stages

There are two scenarios to distinguish: the measurement of an aggregate's reactivity (or that of any other type of component) in relation to the alkali reaction, or the measurement of the dimensional stability of cement based material, made with alkali-reactive aggregate. The quantity of interest is the dimensional variation of the test samples (swelling).

- Qualitative assessment of an aggregate:

The principles used to qualitatively assess aggregates are described in FD P 18 542 [2]. This booklet proposes two methodologies, one based on physio-chemical characterisation of the aggregate (petrographic methods along with chemical analyses), and the other based on dimensional stability tests. Dimensional stability tests involve a long-term test done on standard concrete (see Table 1), or two screening tests, which allow for faster results as long as the test results agree. In the case of standard materials, screening tests may be given preference. In the case of innovative materials, it is preferable to carry out a long-term concrete test.

- Qualitative assessment of a cement material:

Even if a material contains alkali-reactive aggregates, it can be formulated in order to reduce the alkali reaction process, eliminating harmful swelling. It is possible to approve a new product directly using a dimensional stability test (Table 2). These tests involve recording the dimensional variations in material samples over time. After they are withdrawn from the mould, samples are kept in a humid environment and at a temperature above 20°C to speed up the process, if it is to take place. The 38°C test (RILEM [6]) is used as a reference and should be used if there is any doubt about the mechanisms involved. When dealing with conventional mechanisms, it is possible to use the 60°C accelerated test (NF P 18 454 [7]).

In both scenarios, dimensional variations in the samples are influenced by:

- the type of sample:
 - prism size, which should be adapted depending on the test,
 - composition (mortar or concrete),
- the testing conditions:
 - alkali content, with increasing or corrected content, depending on the test
 - temperature, humidity, pressure,

The quantity of interest is the dimensional variation of the test bodies over time. The duration of the test may be adapted depending on the composition of the material being tested.

7. Standard testing methods

Table 1: qualitative aggregate testing

Name	Initial treatment	Preservation	Test duration	Threshold	Comment
NF P18-594 [5] Accelerated test in an autoclave	24 hours, RH=90% 20°C + 48 hours submerged in water at 20°C	5 hours at 127°C, RH=100% P= 0.15 MPa	5 days	Average deformation value.	40x40x160 mm test on standard mortar control screen grid test
NF P18-594 [5] Microbar Test	steam cure: 4 hours in steam at 100°C	alkaline curing: 6 hours at 150 °C in 10% KOH	1 day	Average deformation value.	10x10x40 mm test on standard mortar screen grid test
NF P18-594 [5] Testing on concrete		38°C RH=100%	8 months	Average deformation value	70x70x280 mm long-term test on standard concrete. added alkalis (NaOH added to reach 1.25% Na ₂ O equivalent)

Table 2: testing on concrete

Name	Initial treatment	Preservation	Test duration	Threshold	Comment
NF P 18 454 [7] FD P 18 456 [8]	In moulds at 20 ±2°C for 24 ±2 hours Immersion for 30 ±5 minutes in water at 20 ±2°C.	60 ±2 °C In reactors with an atmosphere of saturated humidity.	Between 3 and 12 months depending on the type of components and the intermediate testing results.	Changes in average values and individual deformation values depending on the type of components	70x70x280 mm Taking into account the components' alkali content variability.
AAR-3 RILEM Method [6, 9, 10]		38°C RH=100%	12 months	Measurement of expansion.	75x75x250 mm addition of alkalis (5.5 kg/m ³ of Na ₂ Oeq)

8. Performance assessment

Assessment method:

- "absolute" assessment: quantity of interest should conform to the thresholds from test NF P 18 454 [7] with interpretation according to FD P 18 456 [8].

9. References

- [1] FD P18-464:2014. Béton - Dispositions pour prévenir les phénomènes d'alcali-réaction, 2014.
- [2] FD P18-542:2015 Granulats - Critères de qualification des granulats naturels pour béton hydraulique vis-à-vis de l'alcali-réaction, 2004.
- [3] N. Baghdadi, Modélisation du couplage chimico-mécanique d'un béton atteint d'une réaction sulfatique interne, ENPC, 2008, pp. 248.
- [4] P. Humbert, A. Dubouchet, G. Fezans, D. Remaud, CESAR-LCPC, un progiciel de calcul dédié au génie civil, Bulletin des Laboratoires des Ponts et Chaussées, Bulletin des Laboratoires des Ponts et Chaussées, (2005) 7-37.
- [5] NF P18-594:2015. Granulats - Méthodes d'essai de réactivité aux alcalis, 2013.
- [6] B - TC 106-3 - Detection of potential alkali-reactivity of aggregates - Method for aggregate combinations using concrete prisms, Materials and Structures, 33 (2000) 290-293.
- [7] NF P18-454:2004. Béton - Réactivité d'une formule de béton vis-à-vis de l'alcali-réaction - Essai de performance, 2004.
- [8] FD P18-456:2004. Béton - Réactivité d'une formule de béton vis-à-vis de l'alcali-réaction - Critères d'interprétation des résultats de l'essai de performance, 2004.
- [9] A - TC 106-2 - Detection of potential alkali-reactivity of aggregates - The ultra-accelerated mortar-bar test, Materials and Structures, 33 (2000) 283-289.
- [10] Rilem TC 106-AAR: Alkali-aggregate reaction, Materials and Structures, 33 (2000) 283-283.

Fact sheet 9

Risk of chemical attacks: acidic solutions

1. Introduction

This sheet covers concrete that is exposed to water or water-saturated soils that contain chemical agents that react with the concrete and lead to the partial or total dissolution of its components. This may mean solutions with low mineral concentrations or highly acidic solutions (mineral acids organic acids), or even solutions containing agents that increase solubility of concrete components (ammonium nitrate, for example). The definition used for aggressive environments is that found in booklet FD P 18-011: 2009 [1], which is a supplement to standard NF EN-206/CN [2].

In the case of water rich in sulphates, the “External Sulphate Attack” fact sheet should be consulted.

This sheet does not cover environments that are acidified due to the presence of a gas such as H₂S in a humid environment, nor does it cover the associated bacterial attacks.

2. Consequences

- Loss of material.
- Loss of cohesion between aggregate and hydrated cement past, aggregate may be dislodged in extreme cases
- When reinforcement is present, its cover is reduced; there is a loss of cohesion between the concrete and the reinforcements, and a loss of load-bearing capacity in cases of advanced degradation.

3. Physiochemical mechanisms

Portland cement based concretes are a typical case of alkaline environments (with a pH of around 13.5 for traditional CEM I-based concrete). If they come into contact with a more acidic environment, ionic exchange occurs by diffusion through the exposed surfaces.

Within the concrete, variations in the interstitial solution lead to a destabilisation of the hydrates in the paste and/or the other component elements of the concrete (aggregate, additives, and fibers). The least stable, i.e. most soluble components are the first to dissolve. For traditional concrete, portlandite (Ca(OH)₂) is the first hydrate to dissolve, followed by the decalcifying calcium silicate hydrates (C-S-H). Limestone aggregate is also susceptible to dissolution depending on the acid's aggressiveness.

Depending on the kind of agents present in the external environment and those present in the concrete, further reactions may occur after following these dissolution reactions:

- Neutralization of the acid by cement hydrates or other concrete components leading to an increased calcium concentration.
- Precipitation of "secondary" compounds, which can slow leaching rate (formation of a protective layer, made of calcite, for example), or accelerate it (as is the case for expansive compounds).

On a micro-structural scale, these kinds of attacks create zones with different compositions, porosities and mechanical properties, which are generally degraded. These zones are delimited by dissolution/precipitation fronts. These zones first appear on the surface and then propagate towards the material's core. In zones with advanced degree of dissolution (zones closer to the surface, zones including most vulnerable components), a total or partial loss of mass is observed.

The thickness of the degraded concrete depends on:

- The material's transfer properties, and in particular the liquid diffusivity, which is measure of how easily the dissolved species move across concrete in question.
- The degree of damage of the material if expansive compounds precipitate.
- The buffering capacity of the material, i.e. its capacity to react with the aggressive agents to limit dissolution reactions (acid neutralisation, precipitation of largely insoluble secondary compounds that can reduce the material's diffusivity).
- The solubility of cement hydrates or other concrete components, which may be modified by the species of the environment.
- The external environment's ability to maintain a certain degree of aggressiveness; for example, solutions that circulate are more aggressive than stagnant water or surrounding soil.

When traditional concrete is in contact with water with a low mineral content, a prevention level similar to that required for protecting against acidic solutions is usually deemed adequate.

Booklet FD P 18-011 :2009 [1] describes the reactions associated with each instance, in particular sections "5.1.2 Acidic Solutions" and "5.1.4 Saline Solutions". The approach varies depending on the country (see BRE-SD1:2005 [3]).

4. Main models

There is no standard model. Nevertheless, research has focused on these subjects and there are models available in the literature:

- specific models for concrete: Adenot [4], Carde [5], de Larrard [6],
- General hydrogeochemical models such as HYTEC[7, 8] or TOUGHREACT [9].

5. Influential parameters

"Material" parameters:

- Presence of concrete components with variable sensitivity to the aggressive solution. This may lead to a heterogeneous advance of the degradation front, for example if the binder becomes soluble more quickly than the aggregates or vice versa.
- Material transport properties.
- Reserve and type of soluble material.
- Ability to form secondary minerals in the environment in question.

"Environment" parameters:

- Solution in contact with the concrete:
 - o Type of compounds present: the booklet FD P 18-011 [1] classifies environmental aggressiveness and recommends concrete composition or any possible additional preventive measure.
 - o Concentration of these aggressive species: the higher the concentration, the thicker the degraded layer of concrete will be.
 - o Frequency of the aggressive solutions renewal: affects the stability of the solution's level of aggressiveness over time by preventing the aggressive compounds from being exhausted and by preventing the accumulation of leaching compounds; the greater the frequency, the thicker the degraded layer of concrete will be (until constant concentrations are maintained).s
- Temperature: increasing temperature accelerates the diffusion of dissolved compounds.

6. Testing method stages

The tests generally involve immersing a sample of concrete in a reactor filled with a solution that approximates the predicted exposure conditions. The important stages are:

- Sample curing length and conditions.
- An inert gaseous atmosphere in the reactor (for example, a flow of nitrogen injected into a solution that has been previously purified with limewater, then with demineralised water to limit concrete carbonation during the test).
- Ratio between the exposed concrete surface and volume of solution.
- Composition and renewal frequency of the test solution that aims to maintain accelerated leaching conditions (a closed reactor whose solution is completely renewed at regular intervals, or an open reactor).
- Temperature: an increase in temperature accelerates the process, according to an Arrhenius law.
- Solution stirring system (magnetic stirrers should be used preferably to avoid creating heat gradients).
- Test duration.

The measured quantities of interest may be:

- Depth of degradation after certain duration of exposure.
- Quantity of acid consumed at constant pH.
- Quantity of dissolved material such as the total quantity of leached calcium or the loss of mass.
- Thickness of the degradation zones (in addition to other quantities), for example through microscope observations.

7. Test solution Standard testing methods

As of 2015, there is no standard test. The table below describes a proposed test. Leaching tests on stabilized waste [10, 11] can be adapted by modifying the solution. It is also possible to use the constant pH leaching test as described in the table below.

Name	Cure	Solution	Quantity	Duration	Comment
Constant pH leaching test [12, 13]	In water saturated with lime for 28 days at $20 \pm 2^\circ\text{C}$.	Nitric acid at 0.25 mol/l (solution renewed at least every 30 ml of acid added). The ratio of exposed concrete surface/solution is determined by the testing method.	- Degraded thickness measured at the end of the test. Quantity of acid added. Quantity of calcium leached.	2 or 4 months depending on the kind of aggregate used	Proposed assessment test to measure the resistance of cement materials to pure water and acids. Precautions should be taken while assessing concrete with limestone aggregates.

8. Performance assessment

Assessment method:

- "Comparative" assessment: the quantity of interest is measured on the candidate concrete, then compared to the values obtained from a standardised reference concrete using the same testing method.
- "Absolute" assessment: there is currently no critical threshold value for the testing method cited above that enables an absolute assessment of service life from test results.

9. References

- [1] FD P18-011:2009. Béton - Définition et classification des environnements chimiquement agressifs - Recommandations pour la formulation des bétons., 2009.
- [2] NF EN 206/CN:2014. Béton - Spécification, performance, production et conformité - Complément national à la norme NF EN 206., 2014.
- [3] BRE SD1:2005. Concrete in aggressive ground., 2005.
- [4] F. Adenot, M. Buil, Modelling of the corrosion of the cement paste by deionized water, Cement and Concrete Research, 22 (1992) 489-496.
- [5] C. Carde, R. Francois, J.M. Torrenti, Leaching of both calcium hydroxide and C-S-H from cement paste: Modeling the mechanical behavior, Cement and Concrete Research, 26 (1996) 1257-1268.
- [6] T. de Larrard, F. Benboudjema, J.B. Colliat, J.M. Torrenti, F. Deleruyelle, Concrete calcium leaching at variable temperature: Experimental data and numerical model inverse identification, Computational Materials Science, 49 (2010) 35-45.
- [7] J. van der Lee, L. DeWindt, V. Lagneau, Application of reactive transport models in cement-based porous media, in: Proceedings of the International RILEM Symposium, Delft, The Netherlands, 2008, pp. 463-470.
- [8] V. Lagneau, J. van der Lee, Operator-splitting-based reactive transport models in strong feedback of porosity change: The contribution of analytical solutions for accuracy validation and estimator improvement, Journal of contaminant hydrology, 112 (2010) 118-129.
- [9] T.F. Xu, N. Spycher, E. Sonnenthal, G.X. Zhang, L.E. Zheng, K. Pruess, TOUGHREACT Version 2.0: A simulator for subsurface reactive transport under non-isothermal multiphase flow conditions, Computers & Geosciences, 37 (2011) 763-774.
- [10] ASTM C1308 - 08. Standard Test Method for Accelerated Leach Test for Diffusive Releases from Solidified Waste and a Computer Program to Model Diffusive, Fractional Leaching from Cylindrical Waste Forms, 2008.
- [11] ASTM C1220 - 10. Standard Test Method for Static Leaching of Monolithic Waste Forms for Disposal of Radioactive Waste, 2010.
- [12] F. Jacquemot, Leaching performance test assessing durability of concrete exposed to chemical attack., in: M.G. Alexander, A. Bertron (Eds.), RILEM Publications SARL, 2009, pp. 372 - 379.
- [13] Méthodologie d'application du concept de performance équivalente des bétons, FNTP - FFB - CERIB - FIB, 2009, pp. 28.