*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

## 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
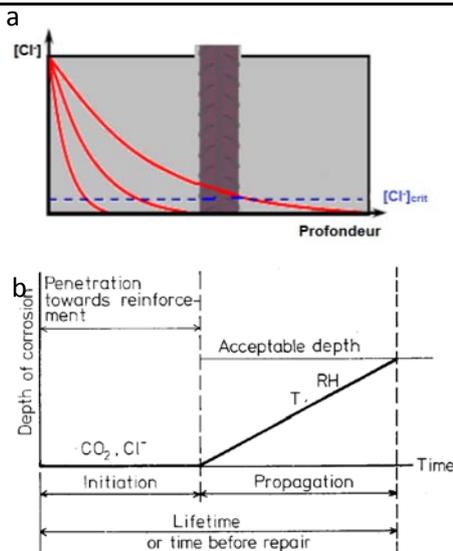
a



b

**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 SDReaM-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.

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

## 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.