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.

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 H_2S 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. it 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 that 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:
    - Type of compounds present: the booklet FD P 18-011 [1] classifies environmental aggressiveness and recommends concrete composition or any possible additional preventive measure.
    - Concentration of these aggressive species: the higher the concentration, the thicker the degraded layer of concrete will be.
    - 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.

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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 ± 2°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

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