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This draft European Standard is for submission to Formal Vote.

If this draft becomes a European Standard, CEN members are bound to comply with the requirements of the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration.

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European Committee for Standardization
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To be corrected later

Foreword

This European Standard has been prepared by Technical Committee CEN/TC 104 "Concrete and related products, the Secretariat of which is held by DIN).

This draft is presented to TC104 SC8 for approval for submission to Formal Vote.

It has been prepared by sub-committee 8 "Products and systems for the protection and repair of concrete structures" (Secretariat AFNOR).

This European Standard is one of a series dealing with products and systems for the protection and repair of concrete structures. It describes a method for determining the depth of carbonation of concrete.

Introduction

Steel reinforcement in concrete may be at risk of corrosion if the concrete is contaminated by chlorides.

ENV 1504-9 defines the principles for protection and repair of concrete structures which have suffered or may suffer damage or deterioration and gives guidance on the selection of products and systems which are appropriate for this intended use. EN 1504-10 requires that the concentration of chlorides be considered when decisions about the removal of concrete are made.

To establish whether there is a risk of corrosion of the steel reinforcement due to a higher chloride content within the concrete than the critical threshold value, the chloride content within the concrete cover and especially at the surface of the steel reinforcement must be determined. Assessment may be made in the field using a variety of rapid test methods, which are not included in this standard.

For accurate determination of chloride content concrete samples must be taken from the structure, prepared for chemical analysis and analysed. For chemical analysis of the concrete with respect to the chloride content either Volhard`s method or potentiometric titration are used as the reference methods.

Alternative methods may also be used when it is clearly shown that these methods result in the same chloride contents as determined by the two standard methods described in this standard.

> NOTE: When alternative methods are used care must be taken to ensure that the chloride levels obtained are not affected by other anions, especially sulphates.

The chloride content may be expressed as a percentage of chloride by mass of cement or of concrete. The chloride content by mass of cement may be derived using either an assumed value for the cement content of the concrete or a value which has been determined by chemical analysis or from construction records.

1 Scope

This standard describes two methods for the determination of the total (free and bound) acid soluble chloride content of hardened concrete or mortar. This information is intended for use in estimating the risk of chloride induced corrosion of the steel reinforcement. It may be used on samples of powder obtained either by drilling or from cores or fragments removed from concrete structures or on other appropriate laboratory specimens.

2 Normative references

This Standard incorporates, by dated or undated reference, provisions from other publications or documents in preparation. These normative references are cited at the appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies.

ENV 1504-9: Products and systems for the protection and repair of concrete structures - Definitions, requirements, quality control, evaluation of conformity - Part 9: General principles for the use of products and systems.

ISO 384 Specification for principles of design and construction of volumetric glassware for laboratory use

3. Materials and apparatus

3.1 Chemicals

- Deionised water with an electrical conductivity less than 2µS/cm,
- Nitric acid (5 mol/l),
- Silver nitrate solution (0,02 mol/l),
- Ammonium thiocyanate (NH_4SCN) solution (0,1 mol/l),
- Ammonium ferric sulfate indicator solution (100 ml of a cold saturated solution of $NH_4Fe(SO_4)_2$ and 10 ml diluted nitric acid),

3,5,5-trimethylhexanol.

NOTE: For the potentiometric method additional reagents may be required as specified by the electrode manufacturer to ensure the proper functioning of the electrode. These will be specified in the manufacturer's instructions for the electrode.

3.2 Apparatus

- crushing and grinding equipment (as required to prepare samples),
- 1,18 mm sieve or smaller,- ventilated oven, controlled to maintain a temperature of 105 ± 5 °C,
- balance capable of weighing up to 5g to an accuracy of 1 mg, - desiccator,
- burette, accurate to 0.05ml,
- 250 ml glass beaker,
- magnetic stirrer,
- heat source,
- vacuum filtering facility (Buchner funnel, filtration flask, medium-textured filter paper),
- 250 ml volumetric flask,
- pipettes accurate to 0,1 ml ,
- if required, potentiometric titration facility (eg. Ag/AgCl electrode or similar, high resistance mV-meter, burette accurate to 0,05 ml or automatic titration equipment.

All volumetric glassware shall be of class A accuracy as defined in ISO 384.

4 Test procedure

4.1 Sampling

4.1.1 Sampling Plan

Sampling shall be in accordance with a plan prepared for the assessment or repair works by a suitably qualified person. When specifying the locations from which concrete is to be removed, specific care shall be taken of the load bearing capacity and reinforcement of the elements to be sampled. The plan shall take into account:

- the size, form, location, orientation, age and structural design of the structure,
- the results of visual surveys and any other available information about possible deterioration,
- the aggregate size and the heterogeneous nature of the concrete,
- exposure conditions, eg. salt water splash zones.

On site checks shall be carried out to ensure that the concrete to be sampled is representative of the elements to be investigated and to confirm the location of reinforcement, which should not be damaged during sampling.

The plan shall specify the approximate number, location and depth of samples, including the depth increments. Typically increments do not exceed 25mm, and it is usual to discard the surface layer.

> NOTE: All holes or damage to the structure from sampling shall be repaired or protected immediately to prevent further deterioration.

4.1.2 Collecting Powder Samples

When collecting drilling for powder samples the diameter of the drilling tool and therefore the number of drill holes required to obtain a sufficient sample size is determined by the by the maximum aggregate size. The powder is collected in separate depth increments, as specified in the sampling plan. A minimum sample size of approximately 1g is required.

> NOTE: A drill diameter of 20mm and two holes is normally sufficient to provide 1g of powder per mm depth of increment. For concrete containing aggregates of maximum size of 20mm a 20mm drill should be used. A sample of at least 20g is normally collected to ensure that it is representative of all of the concrete constituents and not just the aggregate. For larger aggregate sizes a larger drill diameter and sample size should be used.

4.1.3 Taking Core Samples

A core diameter of 30 – 50 mm, depending on the maximum aggregate size, is usually recommended. Larger sizes may be required for large aggregate sizes. Cores shall be marked to indicate their location and orientation with respect to the original concrete surface.

For determination of chloride profiles related to the distance from the concrete surface, the cores may be cut into slices as specified in the sampling plan, without using cooling fluid, or may be ground in increments to obtain powder samples.

4.2 Grinding

Where the sample requires grinding, it shall be dried in an oven to constant weight at 105 ± 5 °C and then allowed to cool to room temperature, for example in a desiccator. When cool it shall be ground to a fine powder to pass a 1,18 mm sieve or smaller, and then homogenised.

4.3 Chemical Analysis

4.3.1 General requirements

The mass of samples shall be given in grams to the nearest 0,001 g and volumes given in millilitres to the nearest 0,05 ml.

Approximately one sample out of every 20 samples (or one sample from every batch if less than 20 samples in the batch) shall be an interlaboratory standard concrete dust specimen of known chloride content. Occasional duplicate analyses, in which the same sample is analysed twice and the results compared, shall also be carried out to confirm the accuracy of the analysis.

> NOTE: In selecting samples for duplicate analyses note should be taken of the results obtained, in particular of any results which fall outside general trends such as a reduction of chloride concentration with sample depth.

4.3.2 Dissolving chlorides

Between 1 and 5g of concrete powder shall be weighed and placed in a 250 ml beaker, wetted with 50 ml water, and 10 ml of 5mol/l nitric acid added, followed by 50 ml hot water.

> NOTE: Adding concentrated acid allows the lab to use a dispenser. This saves time and avoids cross contamination. The addition of hot water quickens boiling and avoids spitting.

The mixture shall be heated until boiling and boiled for at least 3 minutes, stirring continuously.

If necessary the mixture shall be filtered immediately using medium-textured paper, washing the beaker, the stirrer and the residue on the filter.

> NOTE: It is not necessary to filter the solution for potentiometric titration.

4.3.3 Blank Solution

Carry out the same procedure with no concrete test portion.

4.3.4 Determination of Chloride Content

4.3.4.1 Volhard's Method (Method A)

Add 5 ml of silver nitrate solution by pipette into the test solution and stir vigorously to precipitate the chloride.

If the chloride content is high, and a large amount of precipitate is formed, a floculating agent such as 3,5,5-trimethylhexanol may be added. It can be added after the silver nitrate, so the chloride level can be judged from the amount of precipitate formed.

> NOTE: The smell of 3,5,5-trimethylhexanol is overpowering and it is recommended to use it as little as possible.

Add 5 drops of indicator solution and titrate with the ammonium thiocyanate solution one drop at a time, while continually agitating the solution until the faint reddish-brown coloration no longer disappears. Record the volume V_1 of solution used in the titration.

An early end-point, at less than 1ml of ammonium thiocyanate addition, indicates that the test solution demands more silver nitrate solution than the 5.0ml already added. In this case a further 5ml of $AgNO_3$ shall be added and the titration continued until the end point is reached a second time. Record the volume V_1 of solution used to reach the second end point. This procedure may be repeated up to three times. If the sample contains too much chloride then repeat from the beginning (4.3.2) with a smaller sample mass.

Calculate the chloride content as percent of chloride ion by mass of sample using the following formula:

$$3.545 * f * (V_2 - V_1) / m$$

V_1: volume of the ammonium thiocyanate solution used in the titration [ml]
V_2: volume of the ammonium thiocyanate solution used in the blank titration [ml]
m: mass of the concrete sample [g]
f: molarity of silver nitrate solution

4.3.4.2 Potentiometric titration (Method B)

The chloride content is determined with 0,1 M silver nitrate solution in a potentiometric titration. Consumption of silver nitrate solution (V_3) in the titration is noted.

The first derivative method is to be used. First derivative is a technique of adding small aliquots of titrant to the sample, recording the potential changes, and applying a first derivative analysis to the data, from which the endpoint is calculated. The technique assumes that the change in mV reading per volume of titrant added will be greatest at the endpoint.

NOTE: Some instruments work better when a small amount of chloride (equivalent to appr. 0.1 ml of silver nitrate consumption) is added to the sample before digestion. The manufacturer's instructions should be followed.

Carry out the same procedure with a blank solution (with added chloride as for samples if appropriate) and record the volume (V_4) of silver nitrate solution used in the blank titration.

Calculate the chloride content of the concrete as percent of chloride ion by mass of sample using the following formula:

$$3.545 * f * (V_4 - V_3) / m$$

V_3: volume of the silver nitrate solution used in the titration [ml]
V_4: volume of silver nitrate solution used in the blank titration [ml]
m: mass of the concrete sample [g]
f: molarity of silver nitrate solution

5 Test Report

The test report on the determination of the chloride content should include the following information:

a) client's name,
b) date of test,
c) unique sample identification no (and locations of all samples if known),
d) mass, size and type of specimen used (ie. powder, core or fragment),
for dust samples a mass range including lowest and highest mass is satisfactory,
e) chloride content as percent of chloride ion by mass of sample of concrete,
f) chloride content of the interlaboratory standard sample and the accuracy,
g) if requested, chloride content by mass of cement - and how calculated,

NOTE: If requested, chloride content by mass of cement may be calculated, provided that the cement content of the concrete is known; in such a case, the method of establishing the cement content must be given. Otherwise, an estimate based on an assumed value of cement content may be made, but the basis of the assumption must be clearly stated. If the cement content is assumed a value of 14 % cement content is often used for the calculations for a typical normal density concrete. A concrete containing 350kg/m^3 of cement with a density of 2400kg/m^3 has a cement content of about 14% by weight.

h) method of determination (Volhard or Potentiometric),
j) reference to this European Standard.

Any available information on eg. the mix design and age of the concrete should be reported.