CONCRETE, HARDENED:
CHLORIDE CONTENT BY VOLHARD TITRATION

Key words: Hardened concrete, cement, chloride content, chemical analysis

1 SCOPE AND FIELD OF APPLICATION

This Nordtest method can be used for determination of the total chloride content in hardened concrete by dissolving the concrete dust in a solution of nitric acid followed by Volhard titration. Another possibility is to use potentiometric titration which gives better precision and accuracy. This method is not described here.

This Nordtest method does not state in which form the chlorides appear in the concrete or whether or not they are easily dissolved in water.

The method can be used in well-equipped laboratories.

2 REFERENCES

NT BUILD 202 Concrete, hardened: sampling and treatment of cores for strength tests.

3 EQUIPMENT

Core drilling machine or a reciprocating drilling machine, the latter with a diameter of at least 18 mm

Grinder for grinding concrete down to a particle size of less than 0.1 mm

Thermostatically controlled oven for a range of 105 ± 5 ºC

Balance with an accuracy within ± 0.01 g

Glass bottle with a ground glass stopper, holding about 300 ml

Distilled or de-ionized water

Two burettes, each with a volume of 25 ml. One to be used for the silver nitrate solution and the other for the ammonium thiocyanate solution

Gas burner, or similar equipment

Nitric acid (HNO₃), concentrated

- 1 % Nitric acid solution
- Filter, either made from paper or from a material of similar properties
- Filtering flask, 500 ml, with a Büchner Funnel
- Silver nitrate solution (AgNO₃), 0.1 N
- Benzyl alcohol (C₇H₈O) or nonanol-1 (C₉H₂₀O)
- Ammonium thiocyanate solution (NH₄SCN), 0.1 N
- Saturated ammonium ferrisulphate solution (NH₄Fe(SO₄)₂ x 12 H₂O), about 400 g/l.

4 SAMPLING

If the intention is to determine the average content of chlorides in the concrete, one or several test specimens should be selected so that the estimated amount of concrete exceeds about 1 kg. The test specimens may be taken out in connection with cooling in water, for instance according to NT BUILD 202, with the condition that is stated in the test report.

If the intention is to determine the content of chlorides in a certain place in the concrete, e.g. the content of chlorides in a concrete cover layer, then a reciprocating drilling machine should be used and so much of the drill cuttings collected from the actual place in the concrete that the amount of concrete in it may be estimated to exceed about 2 kg.

Preparation of test sample

The drill cuttings do not need to be prepared for a test analysis.

The selected test specimens should be chrushed with a hammer or similar tool to a size that no material is lost.

The chrushed material is then ground in the mill or grinder until a particle size less than 0.1 mm is obtained.
5   METHOD OF TEST

Theory
A solution containing ions of chloride is added to an excess of silver nitrate. The chlorides precipitate as silver chloride.

\[ \text{Ag}^+ + \text{Cl}^- = \text{AgCl} \ (s) \]

The excess of silver ions is titrated with a thiocyanate solution.

\[ \text{Ag}^+ + \text{SCN}^- = \text{AgSCN} \ (s) \]

The excess of thiocyanate ions is indicated by the formation of a red iron(II)-complex.

\[ \text{Fe}^{3+} + \text{SCN}^- = \text{FeSCN}^{2+} \]

Procedure
Weigh the glass bottle. Insert about 5 g of sample into the glass bottle. Dry the sample at 105 ± 5 ºC until no reduction in weight can be seen (minimum 2 hours). Before determining the weight of the dried sample, cool the glass bottle in a desiccator for not more than half an hour.

Add about 20 ml of distilled water and shake the bottle to achieve separation of the particles. Add about 10 ml concentrated nitric acid, shake the bottle, add about 50 ml hot distilled water and shake again. Let the mixture cool for about one hour until it reaches ambient temperature.

Filter the solution and rinse the filter with 1 % nitric acid at least two times. All transitions of liquid should be followed by rinsing, at least twice, with 1 % nitric acid. This is very important to prevent loss of chlorides when you are working with low concentrations.

Add distilled water until all the samples have the same volume.

Add silver nitrate solution in excess from the burette, about 10 ml is sufficient at low concentrations of chlorides.

Add 2-3 ml benzyl alcohol or nonanol and 1 ml saturated ammonium ferri-sulphate solution.

Insert the stopper into the bottle and shake so vigorously that the silver nitrate separates.

Titrate the remaining amount of silver nitrate with the ammonium thiocyanate solution. Shake the bottle vigorously when the end point is near. Continue the titration at a slower rate during a continuously intensive mixing until the solution attains a permanent, weakly red colour.

The content of chlorides (Cl-) is then calculated according to the formula:

\[ \text{Weight} - \%\text{Cl}^- = 3.545 \ \frac{V_1 N_1 - V_2 N_2}{m} \]

\[ V_1 = \text{the added amount of silver nitrate solution (ml)} \]
\[ N_1 = \text{the normality of the silver nitrate solution} \]
\[ V_2 = \text{the added amount of ammonium thiocyanate solution during the titration (ml)} \]
\[ N_2 = \text{the normality of the ammonium thiocyanate solution} \]
\[ m = \text{the weight of the sample (g)} \]

Comments
The solubility product for AgCl is larger than for AgSCN. This means that solid silver chloride can go into solution again when thiocyanate is added.

\[ \text{AgCl(s)} + \text{SCN}^- = \text{AgSCN} + \text{Cl}^- \]

The consumption of thiocyanate becomes too large and the test result is wrong.

To avoid this, add benzyl alcohol or nonanol so that the solid coagulates and the surface gets smaller. The above reaction is only slowed down and the titration with thiocyanate should be done without any delay, especially close to the end point.

Another problem with this method is the lack of a discrete end point. The thiocyanate solution should be standardised against the silver nitrate solution. When titrating to the same colour intensity in all samples, the systematic faults for the standard and the unknown will be identical. The standard should have about the same concentration of chlorides as the sample.

Before the test is carried out both the AgNO₃ and the NH₄SCN solutions should be tested against a chloride solution of known concentration. The AgNO₃ solution should be stored in dark bottles.

Expression of results
The chloride content is expressed with two decimal figures in per cent by weight of concrete.

6   TEST REPORT
If a test report is submitted, it should contain at least the following information:

a) Person who ordered the test
b) Person who performed the test
c) Test method (number and title)
d) Any deviation from the test method
e) Date and identification symbols of the report
f) Date when the test was performed and when the sample was received
g) The state of the samples
h) Test results
i) Any other information of importance for the evaluation of the test results
j) Evaluation of the test results, if this is required in the request for the test
k) Identification and origin of the samples
l) Purpose of the test
m) Date and signature.
1 THEORY
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The excess of thiocyanate ions is indicated by the formation of a red iron(III)-complex.
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2 EQUIPMENT
- Thermostatically controlled oven for a range of 105 °C ± 5°C
- Balance with an accuracy within ± 0.01 g
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- Distilled or de-ionized water
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- Gas burner, or similar equipment
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