Materials and Structures/Matériaux et Constructions, Vol. **35**, November 2002, pp 583-585

RILEM TC 178-TMC: 'TESTING AND MODELLING CHLORIDE PENETRATION IN CONCRETE'

Analysis of total chloride content in concrete

Recommendation

The text presented herafter is a draft for general consideration. Comments should be sent to the TC Chairlady Dr. Carmen Andrade, Institute of Construction Sciences "Eduardo Torroja" (CSIC), Serrano Galvache s/n, 28033 Madrid, Spain. Fax: +34 1 302 07 00; Email: andrade@ietcc.csic.es by 31 May 2003.

CONTENTS

1. BACKGROUND

Reinforcing steel bars embedded in concrete depassivate when a certain amount of chlorides is built up in their surrounding, being the risk for reinforcement corrosion related to the chloride content in the concrete. Therefore, reliable chloride analysis in hardened concrete becomes a key parameter in the evaluation of existing structures and in the prediction of future service life.

The present recommendation is the result of a Round-Robin Test on chloride analysis in concrete, carried out by the Technical Committee TC 178-TMC. A total of 30 laboratories around the world have participated in this RRT and 64 different analyses on triplicate specimens for three different chloride contents have been carried out. The procedure for the analysis of total chloride has been divided in two steps: *extraction* and *quantification*, being able to discriminate the reliability of the procedure followed in each of them. Two different methods of extraction of total chloride from the solid sample as well as six different forms of analysing the resulting liquids have been tested. It was also decided that other methods could also be used to the choice of each laboratory. The complete recipes and results including the statistical analysis can be found in [1]. Other round-robin tests can be found in [2, 3], being presently one the largest ever performed.

As a final result, the method considered to be the most suitable reference for total chlorides (extraction and quantification) is the Volhard method [4-7], which is that described in this recommendation. The ASTM reference method for analysis of total chlorides can be found in [8].

2. AIM AND SCOPE

The present recommendation describes the so-called Volhard Method of analysis (extraction and quantification) of total chloride content in hardened concrete.

1359-5997/02

3. DEFINITIONS

Total chloride content: is the total amount of chloride ion in a sample of concrete, including bound in the solid phases and free chlorides in the pore solution.

Free chloride content: is the amount of chloride ion in the pore solution as obtained by squeezing concrete samples at high pressures.

Water soluble chloride content: is the amount of chloride ion in a sample of concrete which can be extracted by leaching with water at room temperature.

Repeatability (r): is the value below which the absolute difference between two different individual results obtained in the same conditions (same operator, same device, same laboratory and small period of time) is obtained with a probability of 95%.

Reproducibility (R): is the value below which the absolute difference between two different individual results obtained in different conditions (different operators, different device, different laboratories and/or different periods of time) is obtained with a probability of 95%.

4. SAMPLE REQUIREMENTS

The sample must be ground to pass through a 0.16 mm sieve, carefully homogenized and dried at 105-110°C during 24 h. At least two sample portions, about 1 g each, must be weighted to the nearest 0.0001 g, to be tested.

5. MATERIALS AND REAGENTS

5.1. Apparatus

Analytical balance (0.0001 g sensitivity).

Dessicator.

Magnetic stirrers.

Pipette (0.05 ml sensitivity).

Vacuum filtering facility, Buchner funnel, filtration flask (500 cm^3 capacity), and filter paper (20 micrometer pore diameter approximately).

Burette (0.1 ml or higher sensitivity).

5.2. Reagents

All solutions should be prepared with distilled water and p.a. reagents. Concentrated nitric acid is 60% HNO_3 by weight (specific gravity 1.37 g/cm^3).

HNO_3 (1:2)

Mix in a glass container 1 volume of concentrated HNO_3, for instance 200 cm^3, and 2 volumes of water, 400 cm^3. The solution, which must be colourless, is homogenized and kept in a glass bottle.

HNO_3 (1:100)

Pour 15 cm^3 of HNO_3 (1:2) in a glass container with 490 cm^3 of water.

$AgNO_3$ 0.05 M

It is strongly recommended to use a commercially available pre-titrated solution. If not possible, prepare the solution by weighting $AgNO_3$ and dissolving it in distilled water, and standardize it by titration using pure NaCl as a primary standard [4]. Keep the solution in a dark glass bottle.

NH_4SCN approximately 0.05 M

Dissolve 3.8 g of NH_4SCN in distilled water and transfer the so prepared solution quantitatively to a 1000 cm^3 graduated flask. Make up with water, homogenize and keep it in a glass bottle.

$NH_4Fe(SO_4)_2.12H_2O$ indicator

Prepare 100 cm^3 of saturated solution, at room temperature, of $NH_4Fe(SO_4)_2.12H_2O$.

Add 10 cm^3 of HNO_3 (1:2), homogenize the solution and keep it in a dropper bottle.

6. ANALYTICAL PROCEDURE

Weigh with an accuracy of ± 0.0001 g a sample portion of about 1 g in a glass beaker of 250 cm^3, covering it with a watch glass. Add 50 cm^3 of HNO_3 (1:2). When the effervescence has ceased heat the suspension with continuous agitation until it boils for 1 minute. Add 5 cm^3 of the standardized 0.05 M $AgNO_3$ solution by means of a pipette. Allow the suspension to boil for 1 minute more and filter over filter paper, previously washed with HNO_3 (1+100), receiving the filtrate in the 500 cm^3 filtration flask.

Wash adequately the beaker, agitator and filter paper with HNO_3 (1:100). The final volume of the filtrate should be about 200 cm^3.

Allow the filtrate to cool down to room temperature. Add to the filtrate 20 drops of the indicator solution, stir vigorously and titrate with the 0.05 M NH_4SCN solution.

The titration should be stopped when a drop of the thiocyanate solution produces a slight red brown colour, which does not disappear with agitation. Record the spent volume (V1) of the NH_4SCN solution.

If the Cl^- content of concrete is higher than 0.17%, the test should be repeated using a higher volume of 0.05 M $AgNO_3$ solution (for instance 10 cm^3).

Run a blank test using the procedure described above with the same reagents, but without sample. Record the spent volume (V2) of NH_4SCN solution corresponding to the blank test.

Remark: It is necessary to take into account the possible interferences of other ions, for example, $S^=$ which can be avoided by adding H_2O_2.

7. CALCULATIONS

The chloride content in the concrete, expressed as percentage relative to the weight of dry sample (% Cl), is calculated by the following expression:

$$\%\,Cl = \frac{3.5453\,V_{Ag}M_{Ag}\left(V2-V1\right)}{m\,V2}$$

where V_{Ag} is the volume of $AgNO_3$ added (in cm^3),

M_{Ag} is the real molarity of the $AgNO_3$ solution, V1 and V2 are the volumes of NH_4SCN solution (in cm^3) used in the sample and blank tests respectively. m is the mass of the sample portion (in grams).

8. TEST REPORT

The test report must include:

General data:

Identification of the sample (nature, location, sampling date, possible remarks)

Date of the test and location

Name of the person in charge of the test

References about this test procedure.

Results:

Chloride content (Percentage in weight (% Cl)).

9. ACCURACY

The values of repeatability (r) and reproducibility (R) for this method of determination of total chlorides have been determined following the standard ISO 5725-1981 (F), resulting the repeatability is independent of the actual value, with an average of 0.0135. The reproducibility is linearly dependent of the actual value according to the following equation: R = 0.1312 (% Cl) + 0.0152, with a correlation coefficient, r of 0.994.

REFERENCES

[1] Castellote, M. and Andrade, C. *et al.*, 'Round-robin test on chloride analysis in concrete - Part I: Analysis of total chloride content', *Mater. Struct.* **34** (243) (2001) 532-556.

[2] Tritthart, J. and Cavlek, K., 'Determination of total and free chloride in cement paste and concrete', Proceedings of the 2nd International RILEM Workshop on Testing and Modelling the Chloride Ingress into Concrete. Paris, (September 2000) 429-437.

[3] Gulikers, J., 'Reliability of laboratory techniques for chloride analysis of reinforced concrete structures', Proceedings of the 2nd International RILEM Workshop on Testing and Modelling the Chloride Ingress into Concrete. Paris, (September 2000) 439-450.

[4] Basset, J., Denney, R. C., Jeffery, G. H. and Mendham, J., 'Vogel's Textbook of Quantitative Inorganic Analysis', Longman, London, 1978.

[5] Asociación Española de Normalización y Certificación (Spanish Association for Standardization and Certification), Norma UNE 112-010-94, 'Determination of chloride ions in concrete', Madrid, Spain, 1994 (in Spanish).

[6] Asociación Española de Normalización y Certificación, Norma UNE 80-217-91, 'Determination of chloride ions in cements by Volhard's method', Madrid, Spain, 1991, equivalent to the European Standard EN 196-21, 1989 (in Spanish).

[7] EN 1744-1:1998

[8] C114-85. 'Standard Methods for Chemical Analysis of Hydraulic Cement', Ref. Method 19.