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RILEM TECHNICAL COMMITTEES

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

Analysis of water soluble 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 March 2003.

CONTENTS

1. BACKGROUND

As chloride ions in concrete are partially bound with the solid phases, only the so-called free chlorides are a risk of reinforcement corrosion. However, there are experimental difficulties of an accurate measurement of either bound and free chlorides due to: a) their relation is not constant as it evolves with time and temperature, b) there are no reliable analytical methods of quantification of bound chlorides. For free chlorides, it is generally accepted that the squeezing of hardened pastes of concretes gives the best approximation to the chloride ionic concentration existing in capillary pores [1-5]. Due to the complexity of this technique, and to its difficulty to be applied to concrete samples, methods based on leaching have been tried [6, 7].

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 20 laboratories around the world have participated in this part of the RRT, making a total of 37 determinations of free chlorides in triplicate specimens for three different chloride concentrations.

Two different methods of extraction of water soluble chlorides from the solid sample [6] and [7] were tested, taking as *the target values* those obtained by *squeezing* the powdered samples by applying high pressure. It was also decided that other methods could also be used to the choice of each laboratory. The complete recipes and all the results including the statistical analysis can be found in [8]. As a final result, the two methods proposed were considered to be a suitable reference for extracting water soluble chlorides. However, provided that the method given in [6] is easier to perform, it has been considered to take it as the reference method for extraction of free chlorides, and is the only one described in the present recommendation. Experimental description of the leaching with alkaline water method can be found in [7].

2. AIM AND SCOPE

The present recommendation describes a method of analysis (extraction and quantification) of water soluble chloride in hardened concrete based on the extraction with distilled water.

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 0.315 mm sieve. At least two sample portions, about 5 g each, must be weighted to the nearest 0.001 g, to be tested.

5. MATERIALS AND REAGENTS

5.1 Apparatus

Analytical balance (0.001 g sensitivity).

Silver electrode and a reference electrode with an electrolyte free from chloride

Potentiometric titrator

Pipette (0.05 ml sensitivity)

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

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).

Solution of hydrochloric acid (HCl 0.01N), prepared from a commercial standard solution.

Solution of silver nitrate ($AgNO_3$ 0.01N), prepared from a commercial standard solution.

6. ANALYTICAL PROCEDURE

6.1. Water extraction

The following operations must be made in a room at 20 ± 2°C.

Take 5 g of the sample in powder (0.315 mm). Record its exact mass (at ± 1mg) as M_{pe}. Place this sample in a beaker of 250 ml. Add 50 ml of distilled water, and place the beaker during 3 minutes on a magnetic agitating plate. Filter the solution. Rinse only once the beaker with 10 ml of distilled water (this volume has been limited for preventing any supplementary extraction of chloride due to dissolution of calcium chloroaluminates). Add 2 ml of concentrated nitric acid and complement the filtered solution up to 250 ml (V_f) in a graduated flask.

6.2. Analysis

The following operations must be made in a room at 20 ± 2°C.

Determine the exact concentration of the silver nitrate solution (C_{AgNO_3}) with 5 ml (V_{HCl}) 0.01N hydrochloric acid (C_{HCl}) in 50 ml of distilled water. V_t is the volume of silver nitrate added, in millilitres.

Take with a pipette 50 ml (V_p) of filtered solution and pour this volume in a beaker.

Determine chloride content with silver nitrate, in a potentiometric titration. Let V_e in ml be the volume added. The water soluble chloride content, in g per 100 g of sample, is given by Equations (1) and (2).

If the chloride content is very low, an analysis with 50 ml (V_p) of the remaining solution is made after adding V_t = 5 ml of hydrochloric acid 0.01N. Then V_e (in ml) is the volume of silver nitrate added. In this case, the water soluble chloride content, in g per 100 g of sample, is given by Equations (1) and (3).

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 water soluble chloride content in the concrete, expressed as percentage relative to the weight of sample (% Cl), is calculated by the following expressions:

$$C_{AgNO_3} = \frac{C_{HCl}\ V_{HCl}}{V_t} \quad (1)$$

$$\%\,Cl = \frac{3.545\ C_{AgNO_3}\ V_e\ V_f}{M_{pe}\ V_p} \quad (2)$$

$$\%Cl = \frac{3.545\, C_{AgNO_3} (V_e - V_t)\, V_f}{M_{pe}\, V_p} \qquad (3)$$

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:

Water soluble 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). Both parameters are linearly dependent on the actual value of water soluble chloride according to the following equations: r = 0,1391 (% Cl) + 0,0039; R = 0,4334 (%Cl) + 0,0217. The correlation coefficients are of 0.930 and 0.969 respectively.

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