

CHLORIDE IN HARDENED CONCRETE

(An Arizona Method)

SCOPE

1. (a) This method covers the determination of chloride in concrete by a standard addition technique using a chloride electrode. Use of the standard addition technique minimizes the effects of interferences in the samples. "Total Chloride" is obtained by an acid digestion, and "Available Chloride" by water leaching of the concrete sample.

(b) This test method involves hazardous material, operations, or equipment. This test method does not purport to address all of the safety concerns associated with its use. It is the responsibility of the user to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

(c) See Appendix A1 of the Materials Testing Manual for information regarding the procedure to be used for rounding numbers to the required degree of accuracy.

(d) Metric (SI) units and values are shown in this test method with English units and values following in parentheses. Values given for metric and English units may be numerically equivalent (soft converted) for the associated units, or they may be given as rounded or rationalized values (hard converted). Either the metric or English units along with their corresponding values shall be used in accordance with applicable specifications. See Appendix A2 of the Materials Testing Manual for additional information on the metric system.

REAGENTS

2. (a) Chloride standard solution, 1.000 mg/mL, (weigh 1.648 grams dried primary standard Sodium Chloride, and dilute to 1 liter with deionized water).

(b) Nitric acid, 12%. **Caution must be exercised in preparing this solution.** Measure 120 mL concentrated Nitric acid, slowly pour into a 1 liter (1000mL) beaker or flask with approximately 500 mL deionized water. Then, fill with deionized water to make 1 liter solution.

- (c) Deionized water.

APPARATUS

3. Requirements for the frequency of equipment calibration and verification are found in Appendix A3 of the Materials Testing Manual. Apparatus for this test procedure shall consist of the following:

- (a) 300 mL Tall-Form beakers, calibrated to indicate 100 mL volume, with watch glasses.

- (b) An analytical balance capable of measuring the maximum weight to be determined and conforming to the requirements of AASHTO M 231, except the readability and sensitivity of any balance utilized shall be at least 0.001 gram.

- (c) Whatman # 43 filter paper, or equivalent.

- (d) Low temperature hot plate.

- (e) Magnetic stirrer and stirring bar.

- (f) Orion 94-17 chloride electrode with Orion 90-01 reference electrode, or equivalent combination.

- (g) Orion EA 940 specific ion meter, or equivalent.

- (h) 1 mL pipette, accurate to 0.01 mL.

- (i) Thermometer, accurate to at least 0.5 °C.

PROCEDURE

4. (a) Weigh a 1.000 gram representative homogeneous sample of finely pulverized concrete into a beaker. The sample should preferably pass a 75 μm (No. 200) sieve. If " ΔE ", as calculated in paragraph 4(j), is less than 18 millivolts (or if " C_o ", as calculated in paragraph 5(a), is equal to or greater than 0.010 mg/mL), the procedure shall be repeated using a smaller sample, recording the sample weight to the nearest 0.001 gram.

- (b) To the beaker, add 25 mL nitric acid for "Total Chloride" or 25 mL deionized water for "Available Chloride", and cover with watch glass.

(c) Heat at a temperature just below the boiling point for 20 minutes, occasionally swirling solution. Do not allow solution to boil.

(d) Filter into a clean beaker and wash thoroughly using approximately 50 mL of deionized water.

(e) Dilute filtrate to 100 mL with deionized water. This is the "reading solution". Adjust solution temperature to 25 ± 0.5 °C and maintain at that temperature throughout remainder of test.

(f) Place stirring bar in beaker, place beaker on magnetic stirrer, insert electrodes, and initiate stirring. Stirring shall be at a constant moderate rate, such that the vortex created by stirring does not expose the tips of the immersed electrodes. The rate of stirring and the temperature (25 ± 0.5 °C) shall be constant throughout the remainder of the procedure, until the final reading has been obtained in paragraph (i) below.

(g) After reading has stabilized, record initial reading to the nearest millivolt as "E₁".

(h) Add 1.00 mL chloride standard solution.

(i) After reading has stabilized, record final reading to the nearest millivolt as "E₂".

(j) Calculate $\Delta E = E_1 - E_2$.

(k) Repeat steps (b) through (j) on a reagent blank in a clean beaker.

CALCULATIONS AND REPORT

5. (a) Calculate chloride concentration, "C_o" in sample reading solution and "C_b" in reagent blank reading solution, and record each to the nearest 0.001 mg/mL, by the following. (The formula is derived from the Nernst equation for a specific ion electrode. The relation holds in dilute solutions. See Appendix.)

$$C_o \text{ or } C_b = \frac{1}{(101) 10^{\frac{(\Delta E/S)}{59.16}} - 100}$$

Where: $\Delta E = E_1 - E_2$

S = Electrode slope at 25 ± 0.5 °C as determined in accordance with manufacturer's recommendations. (The slope "S" should equal approximately 59 millivolts for a properly functioning electrode. See Section 6, Appendix.)

(b) Calculate percent chloride concentration in concrete, "C" (Total Chloride or Available Chloride), and report to the nearest 0.001%, by the following:

$$C = \frac{10 (C_o - C_b)}{\text{Sample Wt.}}$$

APPENDIX

6. (a) The derivation of the formula for "C_o" and "C_b", the concentration of chloride in the reading solutions, is as follows:

(1) The chloride sensing electrode's behavior is given by the Nernst equation:

$$E = E_o - S [\log (kC)] = E_o - 2.303 \frac{RT}{F} [\log (kC)]$$

Where: E = the measured electrode potential in volts (difference of potential between chloride electrode and reference electrode).

E_o = the standard electrode potential.

S = $2.303RT/F$ = the electrode slope. The theoretical value of "S" is given by:

$$2.303 \frac{8.314 \frac{\text{volt} \cdot \text{coul}}{^\circ\text{K}} 298 \text{ } ^\circ\text{K}}{96500 \text{ coul}} = 0.059 \text{ volt}$$

C = the chloride concentration in the reading solution in mg/mL.

k = a constant which converts concentration to activity.

- (2) For initial reading "E₁" = E₀ - S [log (kC₁)]
 and final reading "E₂" = E₀ - S [log (kC₂)]

$$\Delta E = E_1 - E_2 = S [\log (C_2/C_1)]$$

or
$$\frac{C_2}{C_1} = 10^{(\Delta E/S)}$$

Since
$$C_2 = \frac{C_1 V_1 + C_S V_S}{V_1 + V_S}$$

Where: C₂ = final chloride concentration in mg/mL
 C₁ = initial chloride concentration in mg/mL
 V₁ = initial volume = 100 mL
 C_S = standard chloride concentration = 1 mg/mL
 V_S = volume of chloride standard solution added = 1 mL

then
$$\frac{C_2}{C_1} = \frac{C_1 V_1 + C_S V_S}{C_1 (V_1 + V_S)} = 10^{(\Delta E/S)}$$

or
$$C_1 V_1 + C_S V_S = C_1 (V_1 + V_S) 10^{(\Delta E/S)}$$

or
$$C_S V_S = C_1 [(V_1 + V_S) 10^{(\Delta E/S)} - V_1]$$

Therefore
$$C_1 = \frac{C_S V_S}{(V_1 + V_S) 10^{(\Delta E/S)} - V_1}$$

and
$$C_o \text{ or } C_b = \frac{1}{(101) 10^{(\Delta E/S)} - 100}$$

(b) The formula for "C" (percent "Total Chloride" or "Available Chloride" concentration in concrete) is as follows:

$$C = \frac{[C_o \text{ (mg/mL)} - C_b \text{ (mg/mL)}] (100 \text{ mL}) \left[\frac{1 \text{ g}}{1000 \text{ mg}} \right]}{\text{Sample Weight (g)}} \times 100$$

$$C = \frac{10 (C_o - C_b)}{\text{Sample Wt.}}$$