

- a. Selection of National Institute of Standards and Technology (NIST) Standards:

Select a series of at least four standard cement samples that will bracket the expected concentrations of the elements in the unknown samples.

- b. Preparation of Standards:

Weigh 0.250 g of NIST standard cement into a 100-mL beaker. Disperse with 20 mL of distilled water and 4 mL of concentrated hydrochloric acid. Break up lumps of cement with a rubber policeman or glass stirring rod, rinse and remove the policeman or rod from the beaker. Cover the sample with a watch glass and digest the sample on a low hot plate for 15 min at approximately 75°C. During digestion, continuously stir the sample. An oscillating hot plate is preferred for this process. Filter through a medium-texture filter paper into a 200-mL volumetric flask, scrubbing the beaker with a rubber policeman. Wash the sample thoroughly with hot hydrochloric acid (1:99), then with several rinses of hot distilled water. Cool the sample to room temperature, then dilute to a volume of 200 mL. It is recommended that new standards be made up each month.

- c. Preparation of Samples:

Weigh 0.125 g of cement into a 100-mL beaker. Disperse it with 10 mL of distilled water and 2 mL of concentrated hydrochloric acid. Digest and prepare the sample exactly as described in Section b, "Preparation of Standards." The final filtrate is diluted to a volume of 100 mL.

For the determinations of calcium oxide and magnesium oxide, a portion of the solutions prepared in Sections b

and c are diluted to 1 to 10 with the final dilution containing 0.5 % of lanthanum, which is found to be effective for the suppression of chemical interferences. Standards are diluted similarly.

- d. Preparation of Fly Ash, Pozzolan, and Blended Cement Samples:

Follow the procedures as described in ASTM Designations: C 311 and C 595, except modify the fusion procedure as follows. A quantity of the ignited sample, equivalent to 0.250 g of the moisture free sample, is mixed with 1.5 g of an equal mixture of $\text{Li}_2\text{B}_4\text{O}_7$ and LiBO_2 . The fusion procedure is described in ASTM Designation: E 886. The fused mixture is then dissolved in 80 mL of 1:8 hot hydrochloric acid. The resulting solution is filtered and finally diluted to 200 mL. NIST standards for calibration are prepared in the same way.

- e. Sulfur Trioxide Determination Using an Induction Furnace:

Follow the manufacturer's recommendations. The following has been found to be a satisfactory method using a LECO induction furnace.

Weigh a 0.15 g sample into a combustion crucible. Add one scoop of Lecocel and one scoop of iron chip accelerator. Follow the instrument manufacturer's directions for this analysis. Standardize the instrument with NIST cement standards using the same procedure as described above.

2. Reference Analysis

For silica, ammonium hydroxide group, aluminum oxide, ferric oxide, calcium oxide, magnesium oxide, sulfur trioxide, ignition loss, insoluble residue, sodium oxide and potassium oxide, follow ASTM Designation: C 114.

PART 2. DETERMINATION OF CHLORIDES

This part describes a procedure for determining chlorides in portland cement and portland cement concrete.

A. APPARATUS

1. Chloride specific ion electrode
2. Double junction reference electrode
3. Millivoltmeter compatible with the electrodes

B. PROCEDURE

1. Weigh 2.0 to 5.0 g of portland cement into a 400-mL breaker.
2. Add 100 mL of boiling water.
3. Add a slight excess of 0.1 Normal silver nitrate from a buret (5 mL is an approximate amount of silver nitrate for cement that contains no more than 0.15 % chloride). Record the amount added.
4. Boil the sample for two minutes, remove it from the heat, then cool it slightly.
5. Slowly add 20 mL of concentrated nitric acid, efflorescence will often occur.
6. Heat and break up any lumps of undissolved cement with the flattened end of a stirring rod, cover the sample and boil it for 2 min.
7. Filter through a medium speed (90-mm "OK" is satisfactory) paper in a Buchner funnel with suction. The filtrate should be clear. Add approximately 1 g of diatomaceous earth to aid filtering if desired.
8. Wash the residue three times with 1:99 nitric acid. Discard the residue.

9. Quantitatively transfer the filtrate to a 400-mL beaker and cool it to room temperature.
10. Carry three standards through the test procedures with the same amount of acid and silver nitrate but without cement.
11. Adjust all standards and samples to approximately equal volume with distilled water to eliminate blank determination.
12. Titration of Samples:
 - a. Titration using a ferric ion indicator. With cements that are low in iron, add a few drops of ferric iron indicator (5 g of ferric ammonium sulfate dissolved in 50 mL of 1 Normal nitric acid). Titrate with 0.05 Normal ammonium thiocyanate that has been standardized against the silver nitrate standards to the first permanent red color. Use burets with 0.05-mL graduations and make all readings carefully to the nearest 0.01 mL.
 - b. Titration with a specific ion electrode. Following the manufacturer's recommendation for the use of specific ion electrode, titrate the samples with the 0.05 Normal ammonium thiocyanate that has been standardized against the silver nitrate standards prepared in Step 10. Plot a curve of the change in potential against volume of thiocyanate to find the end point.

13. Calculate chlorides by the following formula:

$$\% \text{ chlorides} = [(A \times N) - (B \times M)] \times F \times 100 / \text{mass of the sample, to the nearest 1g}$$

$$\text{Chlorine (ppm)} = \% \times 10\,000$$

Where A = mL of AgNO_3

N = Normality of the AgNO_3

B = mL of NH_4SCN
M = Normality of the NH_4SCN
F = conversion factor to Cl,
or 0.03546

PART 3. SAFETY AND HEALTH

This method may involve hazardous materials, operations and equipment. This method does not purport to address all the safety problems associated with its use. It is the responsibility of the user of this method to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. This method involves the handling of hazardous chemicals and samples, compressed and flammable gases, and sophisticated instruments which can be dangerous.

Prior to handling testing or disposing of any waste materials, testers are required to read the Caltrans Laboratory Safety Manual

These guidelines pertain to requirements for general safety principles, standard operating procedures, protective apparel, disposal of materials and how to handle spills, accidents, emergencies, etc. Testers are mandated to always observe good hygiene practices. Wash hands after handling samples and before eating, drinking or smoking. Users of this method do so at their own risk.

REFERENCES:

Caltrans Lab Safety Manual
ASTM Designation: C 114
AASHTO Designation: T 105
Portland Cement Association, Research
Department Bulletin 214, "Analysis of Portland
Cement by Atomic Absorption."

End of Test (California Test 404 contains 4 pages)