

A METHOD USED TO DETERMINE CEMENT CONTENT IN CONCRETE

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•THE CEMENT content in hardened concrete must frequently be determined in order to rebut those who tend to blame the cement whenever the concrete does not meet specifications. Although cement failure is indeed a significant factor, other factors that are often overlooked can be equally important. Thus, a method is needed for determining the cement content of hardened concrete so that the possibility of cement failure can be eliminated and other parameters can be examined. Existing methods, which are handicapped by inconvenience, error, or expense, lack the requirements to meet this need.

The standard ASTM Method C 85 (Test for Cement Content in Hardened Portland Cement Concrete), although tedious, usually gives reliable results when information concerning both the cement and the aggregate is available. Kossivas (4) has proposed an alternate method in which the sulfate ion content is determined. However, to obtain a satisfactory cement determination requires that the sulfate content of the cement be known, and that all the sulfates be derived from the cement. The authors have found aggregates, in a number of instances, that contain sulfates in sufficient quantities to cause serious errors.

Some instrumental methods based on neutron activation and isotopic measurement techniques have been used for cement determinations (2, 3). These nuclear methods have been used primarily for field measurements. However, errors caused by common elements exist, as in the previously mentioned methods. Another deterrent is the high cost of equipment.

The method presented in this study is intended to satisfy the need for a method to determine the cement content of hardened concrete and to circumvent the difficulties discussed in existing methods. No prior knowledge of the chemical composition of either the cement or the aggregate is required. The suggested method involves an extraction of the concrete sample with a methanolic solution of maleic acid.

In a previous study (5), maleic acid was used to extract the silicates from portland cement. Subsequently, it was established that all hydration products are soluble in maleic acid. Because the ideal method of determining cement content in concrete would involve a solution of the cement only, maleic acid extraction seemed a plausible approach. This has in fact been confirmed by a study in which a variety of aggregates were extracted by using an alcoholic solution of maleic acid. In no case was aggregate weight loss observed.

EXPERIMENT

Materials Used

Anhydrous methanol and a practical grade of maleic acid are used to prepare 2 liters of 20 percent maleic acid solution. This solution is usable for approximately 2 weeks. Fuller's earth (Matheson Catalog No. L-400) is used as a filtering aid. Filtration is made in a 10-cm Büchner funnel fitted with a tared S and S red ribbon paper. A 200-ml Erlenmeyer vacuum flask is used to receive the filtrate.

The concrete specimens studied are part of a concrete research program. Thus, reliable cement content data are available under a controlled mix design program. A number of cement types were included. Also, a number of mortar cubes made according to ASTM Method C 109 (Test for Compressive Strength of Hydraulic Cement Mortars Using 2-in. Cube Specimens) were analyzed.

Procedure

As illustrated in the block diagram shown in Figure 1, the specific gravity of the concrete is determined first. An adaptation of ASTM Method C 127 (Test for Specific

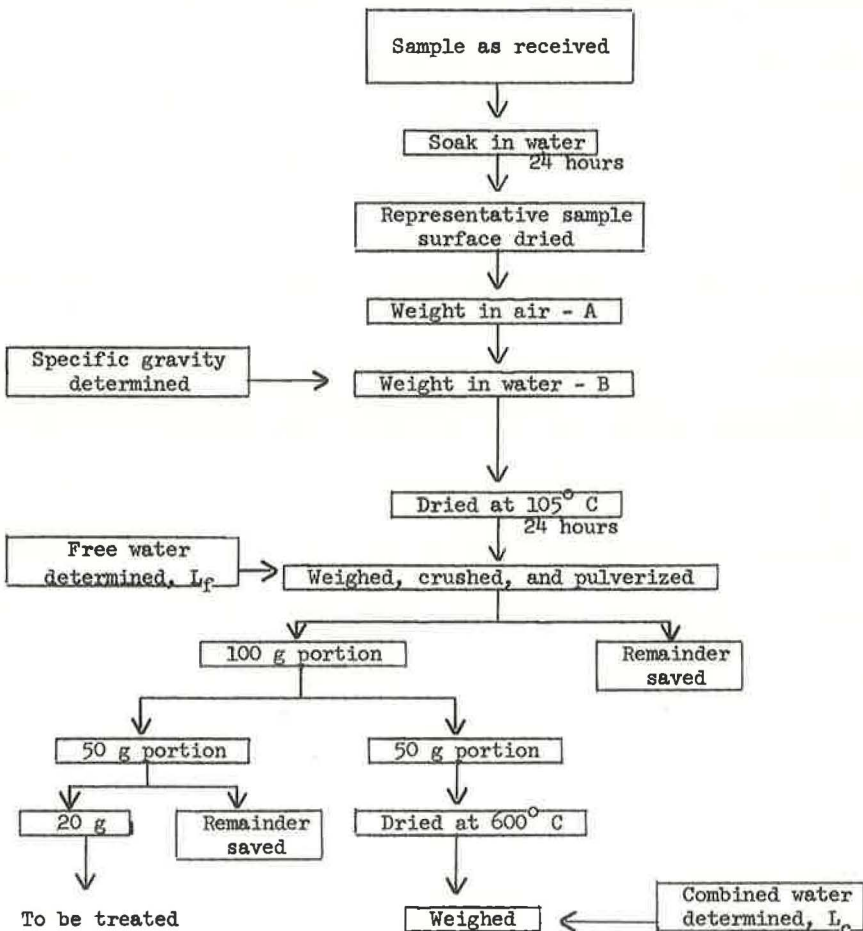


Figure 1. Specific gravity determination and sample preparation of concrete sample.

Gravity and Absorption of Coarse Aggregate) is followed. A sample of the concrete at least 3 times the size of the largest aggregate used in the concrete mix is dried at 105 C to constant weight (overnight is usually sufficient). After soaking for 24 hours, the sample is surface-dried and weighed in air, and then weighed again in water. The bulk specific gravity (saturated surface-dried) is then determined as

$$\text{Bulk sp gr (ssd)} = \frac{A}{A - B}$$

where A = weight in grams of saturated surface-dried sample in air, and
B = weight in grams of saturated sample in water.

At times when speed is essential, a very good approximation of the specific gravity can be made by soaking a sample as received for 1 hour, surface-drying, and weighing as described in the preceding.

If the results are to be incorporated as the content of cement in hardened concrete, the concrete sample should be soaked in water and surface-dried at 105 C for 20 to 24 hours, and the weight loss (L_f) representing the free water in the sample should be calculated.

After the sample has been dried, it is crushed and pulverized to -20 mesh. It is then split to 100 grams. Half of this sample is weighed into a tared dish and dried at 600 C for 4 hours and then weighed and cooled in a desiccator; the loss, L_c , represents combined water.

From the other half of the sample, a 20-gram aliquot is taken for the extraction procedure shown in Figure 2. Three grams of fuller's earth are added with the sample to 800 ml of the maleic acid methanol solution and stirred for 10 min. All but the

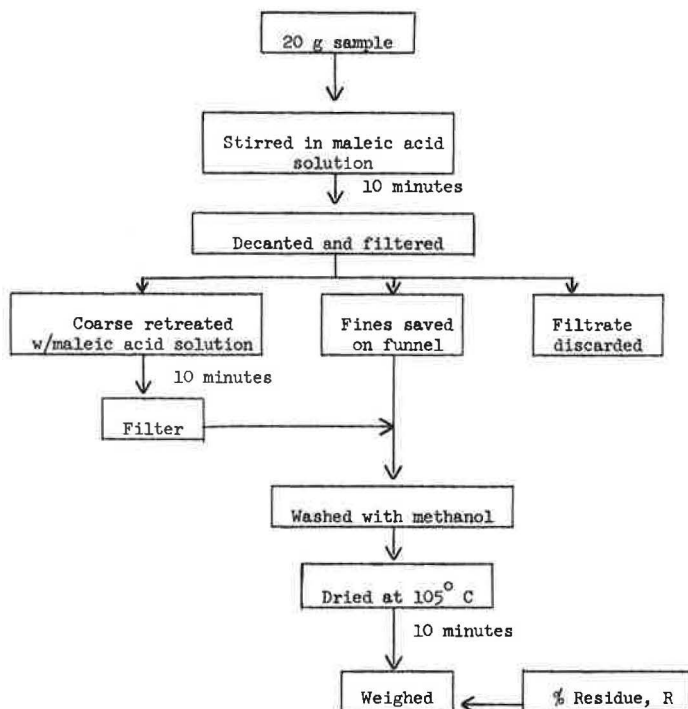


Figure 2. Maleic acid extraction.

coarse particles are filtered through the Büchner funnel. These coarse particles are then re-treated with 400 ml of maleic acid solution, stirred for 10 min, and then washed into the funnel. After the solution has been filtered, the funnel must be carefully washed with methanol to remove all remaining soluble material. The residue is then dried at 105 C for 10 min, cooled in a desiccator, and weighed. The residue, R, is calculated as percentage of residue of the sample.

Calculations

The following calculations give the results of the extraction procedure:

$$L_f = \frac{C - D}{C} \times 100$$

where L_f = free water loss,
 C = weight in grams of saturated surface-dried sample, and
 D = weight in grams of the same sample after 24 hours at 105 C.

$$L_c = \frac{E - F}{E} \times 100$$

where L_c = combined water loss,
 E = weight in grams of pulverized 105 C dried sample, and
 F = weight in grams of the same sample after heating at 600 C for 4 hours.

$$C_p = (100 - R - L_c) \left(1 - \frac{L_f}{100}\right)$$

where C_p = percentage of cement in the concrete, and
 R = percentage of residue.

$$\text{c.c.} = \left(\frac{C_p}{100}\right) \left(\frac{1}{94}\right) (\text{sp gr}) (K)$$

where c.c. = cement content in bags/cu yd; and
 K = conversion factor of metric to English units, 1,685.56.

RESULTS AND DISCUSSION

The cement contents of a large number of hardened concrete specimens have been tested by the maleic acid extraction procedure. The results of some of the tests, representing a number of cement types and concrete mix designs are given in Table 1. In addition, a number of cement content determinations of mortar cubes are given in Table 2.

TABLE 1

COMPARISON OF DETERMINED VERSUS ACTUAL
 VALUES OF CEMENT CONTENT IN HARDENED
 CONCRETE

| Cement Type | Age of Concrete (day) | Cement Content (bags/cu yd) | | |
|----------------|-----------------------------|-----------------------------|------------|------------|
| | | Actual | Determined | Difference |
| II | 23 ^a | 7.0 | 6.7 | -0.3 |
| III | 28 | 6.1 | 5.7 | -0.4 |
| III | 28 | 5.1 | 5.1 | 0 |
| III | 28 | 4.0 | 4.0 | 0 |
| III | 28 | 6.1 | 6.0 | -0.1 |
| I | 7 | 6.0 | 6.0 | 0 |
| I | 7 | 6.0 | 5.7 | -0.3 |
| I | 91 | 6.1 | 5.8 | -0.3 |
| II | 7 | 6.1 | 6.1 | 0 |
| IA | 3 | 6.1 | 5.6 | -0.5 |

^aMonths.

TABLE 2

COMPARISON OF DETERMINED VERSUS ACTUAL
 VALUES OF CEMENT CONTENTS IN MORTAR CUBES
 MADE ACCORDING TO ASTM METHOD C 109

| Age of Mortar (day) | Actual | Determined | Difference |
|---------------------------|--------|------------|------------|
| 1 | 23.6 | 21.9 | -1.7 |
| 3 | 23.6 | 22.1 | -1.5 |
| 7 | 23.6 | 22.0 | -1.6 |
| 28 | 23.6 | 22.1 | -1.5 |

The results given in both tables are shown in Figure 3 where they are expressed as the actual and determined percentages of cement in the total concrete sample. This is a linear relationship that is expressed by

$$Y = a_0 + a_1X$$

where

$$a_0 = 1.135,$$

$$a_1 = 0.885, \text{ and}$$

$$\text{Coefficient of correlation} = 0.99848.$$

From these statistical considerations, it is clear that the correlation is good. The results would be accurate within ± 0.27 bags/cu yd at a 95 percent confidence level when the preceding equation (or curve) is used. Even without the preceding equation, the absolute value determined is very acceptable when one considers the level of precision attained in a field or plant batching operation.

When the age of the concrete is considered, there appears to be no definite trend in the concrete results given in Table 1. By contrast, the mortar cubes (Table 2) do show a trend where the negative bias diminishes with age. This is attributed primarily to the slow hydration rate of the ferrite phase of portland cement. The calcium silicates are readily soluble in methanolic maleic acid, whereas the aluminates and ferrites are normally insoluble. However, in an aqueous phase, the aluminates hydrate rapidly and become soluble in the maleic acid solution, leaving only ferrites in the residue.

The difference between the actual and the experimental cement contents in the mortar cubes, expressed as percentage of unhydrated C_4AF versus time of curing, is shown in

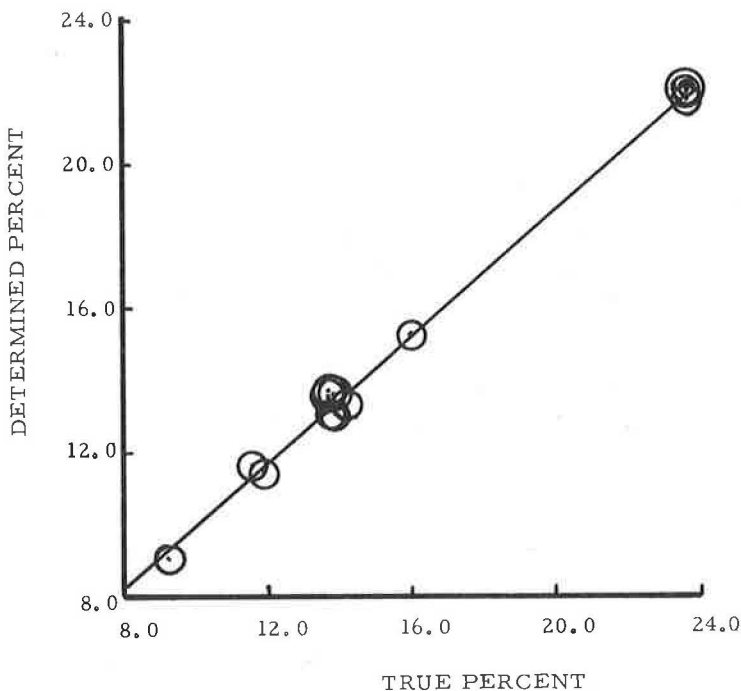


Figure 3. A linear regression line of determined and actual percentages of cement content in total concrete sample.

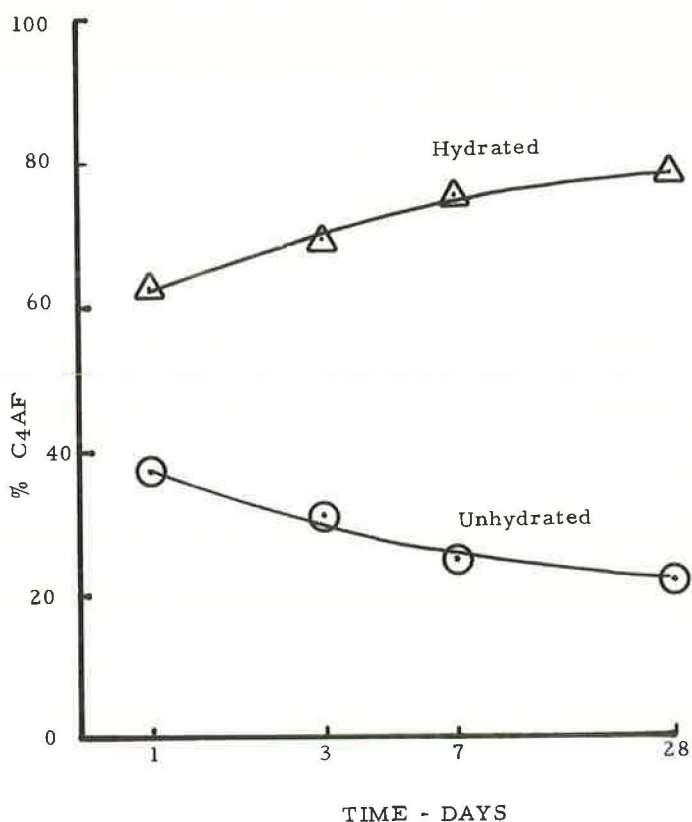


Figure 4. Differences between actual and determined values of cement content in mortar cubes (hydrated curve is obtained by difference).

Figure 4. This plot clearly shows that these differences are a function of the hydration rate of the ferrite phase. It is interesting to note the reaction rate, as shown by the hydration curve in Figure 4. This rate seems to be in general agreement with the results reported by Copeland et al. (1) in their study of the reaction kinetics of cement compounds. Because the hydrated ferrite phase is also soluble, the only insoluble fraction of the cement left after an extraction is the unhydrated ferrite phase. An X-ray diffraction study of the extracted residue lends further support to this conclusion. Unfortunately, the amount of unextracted ferrites is so highly diluted with the other insoluble residues that it was found impractical to determine its amount by a quantitative X-ray diffraction method.

Although the methanolic maleic acid will leave nearly all igneous and calcareous aggregates unaffected, it will probably give erroneously high values when pozzolanic materials are included in the concrete.

REFERENCES

1. Copeland, L. E., Kantro, D. L., and Verbeck, G. Chemistry of Hydration of Portland Cement. Research and Development Laboratories, Portland Cement Association, Bull. 153.
2. Covault, D. O., and Poovey, C. E. Use of Neutron Activation to Determine Cement Content of Portland Cement Concrete. HRB Bull. 340, 1962, pp. 1-29.

3. Iddings, F. A., Arman, A., Perez, A. W., II, Kiesel, D. W., and Woods, J. W. Nuclear Techniques for Cement Determination. Highway Research Record 268, 1969, p. 118-130.
4. Kossivas, K. G. Cement Content Determination in Hardened Concrete. Rock Processing Chemical Research Seminar, W. R. Grace and Company, Chicago, March 6, 1969.
5. Tabikh, A. A., and Weht, R. G. A Study of Portland Cement by X-Ray Diffraction. 21st Pacific Coast Regional Meeting, American Ceramic Society, Oct. 1968.