

Determination of Cement Content of Soil-Cement Mixtures

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Rapid and accurate determination of the cement content of soil-cement mixtures and cores becomes increasingly important with advanced construction techniques and improved designs. This paper covers an investigation and evaluation of six methods of test currently in use by various agencies. These methods are: (a) ASTM Designation D806 - 57; (b) Versene method; (c) flame photometer method; (d) California method; (e) conductivity method; and (f) chemical analysis method.

The results indicate that all the test methods investigated could be utilized but that certain methods are more desirable than others for particular conditions. This investigation indicates that either the California or the conductivity method of test would be the most practical for field use and that the ASTM, Versene or the California method would be suitable for most laboratory requirements. (Cement contents throughout this paper are expressed as percent weight of dry soil.)

•WITH increasing use of soil-cement in Canada, many agencies have realized the need for a fast and accurate method of determining the cement content of the mix. In 1960, the Alberta Department of Highways began a laboratory investigation to determine the most suitable method of cement content determination for their particular needs. To correlate field data with laboratory design, it was necessary to determine the percentage of cement present in field cores.

The investigation was carried out on six different methods currently being used to determine the cement content of soil-cement mixtures.

ASTM PROCEDURE

In the ASTM procedure (Designation D806 - 57), chemical analysis is employed to determine the cement content of samples of soil-cement mixtures either during or after construction. Samples of the raw soil, cement, and soil-cement mixture must be obtained and analyzed. Hydrochloric acid is added to each sample and the resulting precipitate discarded. The remaining filtrate is made slightly ammoniacal and the hydroxides are allowed to settle out. The precipitate is washed with ammonium nitrate and the hydroxides are dissolved with hydrochloric acid. The solution is again made slightly ammoniacal, the precipitate washed with ammonium nitrate and the hydroxide precipitate discarded. Ammonium hydroxide is added to the filtrate, the solution is heated and ammonium oxylate is added. The calcium oxylate is filtered off, washed into a beaker, diluted, and sulfuric acid then added. This is then titrated with a standard potassium permanganate solution.

The above procedure is carried out for the three samples (raw soil, cement and soil-cement mixture) and the cement content then computed by means of the following formula:

$$\text{Cement content (\%)} = \frac{J - I}{5H - I} \times 100$$

in which

H = potassium permanganate (KMnO₄) solution required for titration of cement sample, ml;

I = KMnO₄ solution required for titration of the raw soil, ml; and

J = KMnO₄ solution required for titration of the soil-cement, ml.

VERSENE METHOD

The Versene method is recommended for all soils except those containing a large or variable amount of calcium. It is recommended by the British Road Research Laboratory for most purposes, including field tests, and results can be obtained in appreciably less time than with the ASTM method. This method can also be used for determination of the lime content of soil-lime mixtures.

The cement content is estimated by measuring the combined calcium and magnesium contents of the natural soil, the stabilized soil, and the cement. Titration is performed with the disodium salt of ethylene-diamine tetracetic acid (EDTA). Filtrations are eliminated but since the soil, cement and soil-cement mixture are analyzed separately, the errors introduced are largely canceled out.

Hydrochloric acid is added to the samples to dissolve compounds of calcium, magnesium, iron, aluminum, etc., and then ammonium hydroxide is added to an aliquot portion until red litmus turns blue. The hydroxides of iron, aluminum, and titanium are precipitated out, if present, while the calcium and magnesium stay in solution. An aliquot portion containing the calcium and magnesium in solution is then titrated with EDTA using eriochrome blue-black as an indicator until all traces of pink have disappeared.

FLAME PHOTOMETER METHOD

The flame photometer method is preferable to the two previous ones where a large number of determinations are required on the same soil sample and time is an important factor. The equipment necessary for the test is, however, fairly expensive and a supply of gas, electricity, and compressed air is required.

The method involves initial calibration of the photometer followed by spraying a portion of the processed soil-cement solution through the photometer.

CALIFORNIA METHOD

The California method for finding the cement content of freshly mixed soil-cement is based on chemical titration methods which relate the cement concentration of samples to known solution concentrations. Two types of titrations are performed: an acid-base titration and a constant neutralization method. The acid-base titration is used when the aggregates do not react with hydrochloric acid and the constant neutralization method is used when there is a reaction.

The acid-base test is based on the neutralization of the cement with an excess of hydrochloric acid. The residual excess acid, as measured by back titration with an alkali, is inversely proportional to the cement content of the soil-cement mixture.

The constant neutralization procedure is based on the continuous neutralization of an aqueous solution from the cement-treated aggregate specimen for a specified period of time. This is accomplished by adding just sufficient acid to neutralize the OH ion that is continuously being liberated during hydration of the cement. The amount of acid used is directly proportional to the cement content of the soil-cement mixture.

CONDUCTIVITY METHOD

The conductivity method (Washington State Highway Commission) is based on the change of conductivity of water with the addition of cement. Suitable calibration curves

are first obtained by measuring the conductivity of diluted mixtures containing a known percentage of cement. The cement content is then determined by measuring the conductivity of the diluted sample and referring to the standard calibration curves.

The method of test is quite inexpensive and may be used in the field as well as in the laboratory, but there are several aspects of procedure that must be carefully controlled to insure accurate results. Some of the factors which may or may not have an appreciable effect on results are as follows:

1. Use of field water supply instead of distilled water;
2. Type of cement or aggregate;
3. Sample size and grading;
4. Length of tempering time (4);
5. Length of dilution time;
6. Amount of dilution;
7. Effect of agitation; and
8. Temperature.

CHEMICAL ANALYSIS METHOD

The chemical analysis method is essentially the same as the ASTM procedures except for the following points. The iron and aluminum are not precipitated but just the calcium in the form of the oxylate. The hydrochloric acid is neutralized with ammonium hydroxide and acetic acid added to decrease the pH from 7 and thus leave the iron and aluminum in solution. An excess of ammonium oxylate is then added to the calcium to give a precipitate of calcium oxylate. The procedure then continues as for the ASTM procedure.

TEST PROGRAM

Work on the test program was carried out from 1958 to 1961 and comprised the following phases:

1. Comparison of the ASTM and Versene methods of test on laboratory samples of known cement content (summer and fall 1958);
2. Comparison of results obtained by ASTM and Versene methods on field specimens consisting of both formed specimens and cores of soil-cement;
3. Comparison of results obtained by experienced and inexperienced technicians using the Versene test method (1959);
4. Comparison of results using ASTM, Versene, chemical analysis and conductivity methods of test (conductivity tests performed by Alberta Research Council);
5. Comparison of results using California method and chemical analysis method on a prepared sample of known cement content; and
6. Comparison of the six methods of cement content determination to evaluate suitability for the particular requirements.

RESULTS AND CONCLUSIONS

Table 1 gives a comparison between cement contents from the field and those obtained by the Versene method in laboratory test. The cement content from the field was an average value for the day, and the cement content of samples obtained for the laboratory tests could have varied appreciably from this average. The laboratory result was considerably lower than the field result in most cases except for the Updike Lake material where the field control was difficult to obtain and results may not be completely reliable. The soil-cement samples tested consisted of a fine sand of the dune sand type for the Reaume, Elhardt and Ravenshaw pits, a coarse well-graded sand for the Sheppert pit and a crushed sandstone for the Updike Lake pit.

The results of a comparison of the ASTM and the Versene methods (Table 2) show that both methods of test give sufficiently accurate results for either field or laboratory usage. The Versene method appears to give slightly higher values than the ASTM

TABLE 1

COMPARISON OF FIELD ESTIMATED CEMENT CONTENT AND LABORATORY CEMENT CONTENT (Versene Method), 1959

Pit Name	Sample No.	Lab. Cement (%)	Field Cement (%)
Reaume ^a	44102	9.3	10.7
	44106	11.1	10.8
	44108	9.7	13.3
	44104	11.1	—
	44254	10.8	11.0
	44259	10.4	11.2
Updike Lake ^b	44134	12.8	10.9
	44138	14.6	13.4
	44142	21.1	13.2
	44144	19.2	13.2
	44146	12.5	17.0
	44152	13.8	12.0
	44116	9.6	6.0
	44118	15.8	10.5
	44126	15.8	11.0
	44128	10.4	12.1
	44130	12.8	8.4
	Elhardt ^c	43465	4.9
43467		7.1	8.0
43832		5.3	8.0
Ravenshaw ^d	43732	7.3	9.0
	43734	6.8	9.0
	43736	8.1	9.0
	43738	6.4	9.0
	43740	8.6	9.0
	43742	6.2	9.0
	43744	6.6	9.0
	43746	6.2	9.0
	43748	10.5	9.0
	43750	12.4	9.0
	43839	10.0	9.0
Sheppert ^e	44572	7.9	10.5
	44578	4.0	9.0
	44582	3.8	6.8
	44584	6.6	6.7
	44586	5.8	7.0
	44590	5.3	7.0
	44594	7.1	7.0

^aProject 2-K-2
^bProject 2-K-2
^cProject 12-B-1

^dProject 12-B-1
^eProject 28-B-2

TABLE 2

RESULTS OBTAINED FROM THE ASTM AND VERSENE METHODS, 1959

Sample	Cement Content (%)		
	Standard	ASTM Method	Versene Method
1	6 ^a	6.0	5.8
2	8 ^a	7.9	8.0
3	10 ^a	9.9	10.0
41166	9.0 ^b	9.2	9.7
41186	9.0 ^b	10.4	10.7
41200	9.0 ^b	9.4	10.6
41196	9.0 ^b	10.0	11.3
41575	9.0 ^b	5.5	6.3

^aKnown.

^bUnknown (approximate).

method which may be due in part to small quantities of aluminum or iron being present which are taken as calcium in the Versene determination. It may also be due to a poor end point obtained in the titration process.

The comparison of results obtained with experienced and inexperienced personnel using the Versene method of test (Table 3) definitely indicated the need for experienced personnel. A good knowledge of quantitative chemistry plus knowledge of the physical and chemical properties of cement must be combined with good laboratory technique to insure accurate results.

Table 4 compares results using the ASTM, Versene, chemical analysis and conductivity methods. On the basis of the limited data available, the Versene and conductivity methods appear to give the best average value of test. The ASTM method appears to give a slightly low value of test and the chemical analysis method a slightly high value. However, it is felt that considerably more investigation and test data would be required to substantiate or disprove these findings.

Table 5 indicates that the California method gives excellent results when checked against a known admixture content, whereas the chemical analysis method again indicates results slightly on the high end of the scale. However, test data to verify this indication are very limited.

TABLE 4
RESULTS USING VARIOUS METHODS
FOR DETERMINING CEMENT
CONTENT, 1960

Sample No.	Cement Content (%)			
	ASTM Method	Versene Method	Chemical Analysis	Conductivity Method
53797	6.6	7.6	8.3	
53801	4.4	5.6	6.7	
53804		8.2	8.6	
53805	6.4	7.5	8.1	
54521	7.1	6.3	7.5	6.5
54522	7.9	8.7	8.1	7.8
54526	6.2	6.8	8.4	7.4
54528	5.8	6.4	8.4	7.0
54523		11.0 (?)		7.4
54524		10.9 (?)		7.5
54525		11.5 (?)		8.3
54527		11.1 (?)		7.5
54529		9.2 (?)		7.3

TABLE 3
RESULTS OBTAINED WITH EXPERIENCED AND INEXPERIENCED TECHNICIANS (Versene Method), 1959

Sample No.	Cement Content (%)	
	Experienced	Inexperienced
1	8.7	8.5
2	9.5	9.6
53797	7.6	14.8 13.0 11.0 10.8
53801	5.6	12.2 10.4 9.0 8.8
53802		10.0 8.3
53804	8.2	8.1 8.3 7.1 6.9
53805	7.5	15.1 13.9 11.9 11.7
54521	6.3	13.3 11.0 10.0 9.5
54522	8.7	11.5 12.3 10.7 10.3
54526	6.8	13.8 10.1 6.2 6.1
54528	6.4	13.7 13.2 11.9 10.8

TABLE 5
COMPARISON OF RESULTS FROM
CHEMICAL ANALYSIS AND
CALIFORNIA METHOD

Sample No.	Cement Content (%)		
	California Method	Chemical Analysis	Known Admixture Content (%)
1	5.0	6.9	5 ^a
2	9.7	11.5	10 ^a
3	11.0	12.7	10 ^b

^aCement.
^bLime.

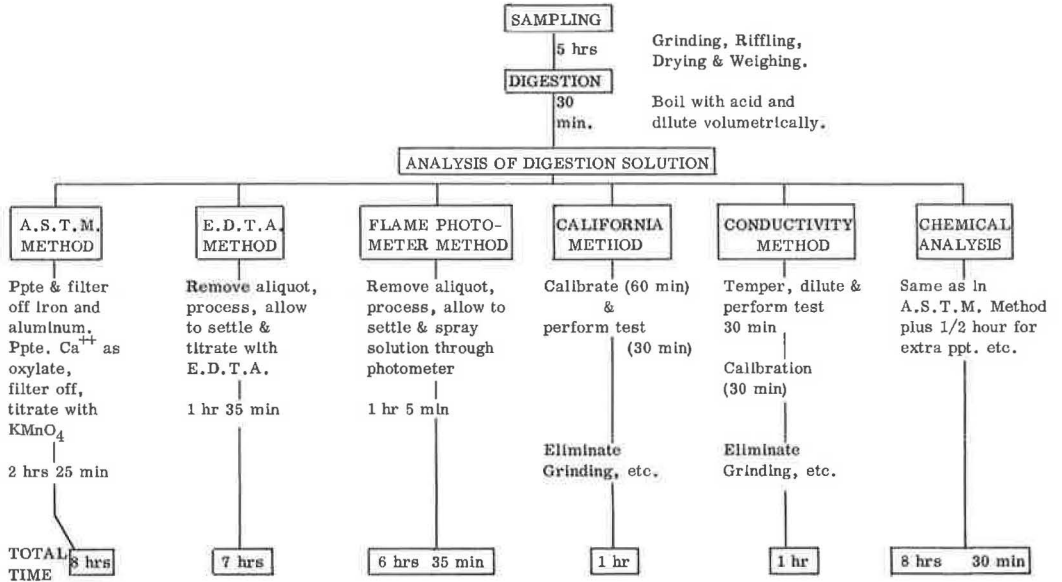


Figure 1. Time required for determination of cement content of soil-cement mixtures by six methods of analysis.

TABLE 6
COMPARISON OF VARIOUS METHODS OF CEMENT CONTENT DETERMINATION OF SOIL-CEMENT MIXTURES

Property	ASTM	Versene	Chemical Analysis	Conductivity	Flame Photometer	California
Speed	5	4	6	1	3	2
Accuracy	2	1	4	1	3	2
Initial cost of equipment	2	1	3	5	6	4
Training of technicians	5	4	6	1	3	2
Space required	3	3	3	1	2	2
Portability	4	3	5	1	6	2
Maintenance cost	5	4	6	1	3	2
Supervision required	4	3	5	1	5	2
Computations	5	4	6	1	3	2
Reproducibility of results	5	4	6	3	2	1
Technician's safety	5	3	6	1	2	4
Availability of utilities	3	4	5	1	6	2

Figure 1 compares the time required in the various methods of test to determine cement content of a soil-cement mixture. Information obtained during the local investigation is substantiated with that from reference material. The California and the conductivity methods require much less time to run inasmuch as the time of grinding, riffing and drying has been eliminated. The time required for the calibration of apparatus has not been included in these two methods but in any event they would take less than one-quarter the time of the other test methods. This time factor plus the indicated accuracy of these two test methods certainly makes them worthy of further investigation.

Table 6 was prepared to show the relative merits of each type of test and to serve as a guide in choosing a test method for a particular purpose. Preparation was to a large extent from noted reference material as personal experience has not been sufficient to permit accurate appraisal of all list methods. The following points are indicated:

1. After calibration of the equipment, the conductivity, flame photometer and California methods are appreciably faster than other methods of test;
2. The ASTM and Versene methods appear to be most accurate, while the chemical analysis method appears to give slightly high results; however, all methods appear to be sufficiently accurate for job control purposes; and
3. In practically all other ways noted, the conductivity and California methods of test appear to be most suitable for use.

The ASTM and Versene methods are rated low in this comparison on the basis of reproducibility of results because trained and experienced technicians are required. Comparisons in general are on the basis of tests carried out by relatively unskilled technicians, who might be found in the average testing laboratory.

In Table 6, number 1 in each case represents the most desirable method; number 6 represents what is considered to be the poorest. For example, the fastest method is rated as number 1; the slowest method as number 6.

Items which may have an important bearing on the general test results are listed below.

1. Relatively small samples are used in the ASTM, Versene and Chemical Analysis methods of test and segregation or poor sampling of materials could therefore have an appreciable effect on the test results.
2. The ASTM method required a double precipitation to be performed and it is considered that there is a possibility of losing calcium or having a portion of the ferrous iron and aluminum stay in the precipitate, which would give erroneous results. In cases where the soil contains an appreciable amount of these materials, the error could perhaps become significant. The Versene method of test reacts the same way and here the error could possibly be even greater.
3. In the Chemical Analysis method, the iron and aluminum is not precipitated but only the calcium in the form of the oxylate. The hydrochloric acid is carefully neutralized with ammonium hydroxide and the pH decreased from 7 by the addition of acetic acid to leave the iron and aluminum in solution. An excess of ammonium oxylate is then added to the calcium to give a precipitate of calcium oxylate. The procedure from this point is identical to the ASTM method.
4. The ASTM, Versene and Chemical Analysis methods of test require test equipment such as an analytical balance, electric oven, dessicator and glassware and are therefore relatively expensive tests to set up in the field. In contrast, the California method uses plastic ware which is an advantage.
5. The Flame Photometer method requires experienced, well trained technicians and the equipment has a high initial cost.
6. The end point in titration is much more distinct for the Chemical Analysis than for the ASTM or Versene methods. This could possibly be improved in the California method by titrating 25 ml of solution rather than 100 ml.
7. The Conductivity method could possibly require frequent re-calibration of the equipment as slight vibration or jarring of the equipment may give sufficient change to the conductivity cell to alter results. In addition, the technician must know the electric circuits involved and have a knowledge of chemistry.

On the basis of the above, it would appear that, of the methods investigated, the California or the Conductivity method would be the most practical for field use. In the main laboratory, the ASTM method, the Versene method or the California method would probably be most suitable. These test methods also permit determination of the lime content of soil-lime mixtures and can be used for hydrated or unhydrated soil-cement.

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Appendix

PROCEDURE¹ FOR HIGHWAYS TESTING LABORATORY, EDMONTON, CANADA

Test Method

1. Weight out, on the analytical balance the following amounts of the samples:

Raw soil, 5,000 g
Soil-cement mixture, 5,000 g
Cement, 1,000 grams²

Place the materials in a 250-ml beaker.

¹ Adapted from ASTM Procedure D806 - 57.

² Exact weights of 5,000 g for the samples of soil and soil-cement and 1,000 g for the sample of cement do not have to be used. This will save time in weighing. If exact weights are not used then the following corrections must be made:

$$I^1 = \frac{I(5)}{\text{Wt. Used}} \quad J^1 = \frac{J(5)}{\text{Wt. Used}} \quad H^1 = \frac{H(1)}{\text{Wt. Used}} \quad \% \text{ Cement} = \frac{(J^1 - I^1)}{5H^1 - I^1} \times 100$$

2. (a) Add 50-ml HCL (1:1) to the soil and soil-cement.
(b) To the cement add 40-ml water. Stir into a paste. Then add 10-ml concentrated HCL (Sp. Gr. = 1.18).
3. Cover and boil gently for 5 minutes.³
4. Add 25-ml hot water. Stir, allow to settle through a Whatman No. 1 filter paper, preferably 15 cm in diameter. If the filtration period exceeds one hour, substitute a No. 41 paper in subsequent similar cases.
5. Receive the filtrate in a 250-ml volumetric flask.
6. Wash the residue once by decantation using hot water, then transfer it to the filter paper.
7. The beaker should be rapidly policed, the loosened material being transferred to the filter paper.
8. Wash the material on the filter 4 times with hot water (use about 10 to 15 ml each time).
9. Discard the filter.
10. Dilute the filtrate in the volumetric flask to 250 ml with cold water and mix the contents by agitating.
11. Using a 50-ml pipette remove a 50-ml aliquot into the original 250-ml beaker.
12. Dilute to about 100 ml.
13. Make the solution slightly ammoniacal by adding NH_4OH . (Put a small piece of red litmus paper into the beaker; stop adding NH_4OH after the litmus paper has turned blue.)
14. Boil 1 to 2 minutes and then allow the hydroxide to settle.
15. Filter through an 11-cm Whatman No. 1 filter paper.
16. Receive the filtrate in a 600-ml beaker.
17. Wash the original 250-ml beaker into the filter with hot NH_4NO_3 (20 g per l) once. Follow by washing the hydroxide precipitate once or twice with hot NH_4NO_3 (20 g per l).
18. Set the filtrate aside (in the 600-ml beaker).
19. Transfer the paper and precipitate to the original beaker. Add 20-ml hot HCL (1:3) and then add 50-ml water.
20. Make the solution slightly ammoniacal (as in 13) and boil 1 to 2 minutes.
21. Allow the precipitate to settle.
22. Decant through a Whatman No. 1 filter paper, receiving the filtrate in the 600-ml beaker containing the first filtrate (previously set aside).
23. Wash and police the 250-ml beaker in which the precipitation took place.
24. Wash the precipitate on the filter paper 3 or 4 times with NH_4NO_3 (20 g per l).
25. Discard the hydroxide precipitate (on the filter paper).
26. Add 2-ml concentrated NH_4OH (Sp. Gr. 0.90) to the filtrate (which will now have a volume of 250 to 350 ml).
27. Heat the solution to boiling.
28. Add 10-ml hot saturated $(\text{NH}_4)_2\text{C}_2\text{O}_4$ (ammonium oxalate) solution.
29. Keep the mixture near boiling until the precipitate becomes granular.
30. Set aside the beaker on a warm hot plate for 30 minutes or more.
31. Before filtering off the CaC_2O_4 (calcium oxalate) precipitate, verify completeness of precipitation by adding a little more $(\text{NH}_4)_2\text{C}_2\text{O}_4$. If the solution remains clear then precipitation is complete. Make sure that a slight excess of NH_4OH is present. (Dip a stirring rod into the solution and put a drop of it on some red litmus paper, which will turn blue if there is an excess of NH_4OH .)
32. Filter through an 11- or 15-cm Whatman No. 2 filter paper, making sure that all the precipitate is being retained.
33. With a rubber policeman clean the 600-ml beaker in which precipitation took place and transfer the contents to the filter with a stream of hot water.
34. Wash the precipitate on the filter 6 to 10 times with a stream of hot water (not over 75 ml).

³Vigorous or extended boiling of samples is seldom necessary and often results in much slower filtration.

35. Carefully open the filter paper and wash the precipitate with water into the 600-ml beaker (where precipitation was effected). Save the filter paper.
36. Dilute to 200 ml.
37. Add 10-ml H_2SO_4 (1:1).
38. Heat the solution short of boiling and titrate it with KMnO_4 solution to a persistent pink color. (The KMnO_4 solution need not be a standard solution, but the same solution shall be used in titrating all the components.)
39. Add the filter paper and macerate it.
40. Continue the titration slowly until the pink color persists for 10 seconds.
41. Record the volume of KMnO_4 used.

Calculation:

$$\% \text{ Cement} = \frac{(J - I)}{5H - I} \times 100$$

in which

- H = KMnO_4 solution required for titration of the sample of cement, ml;
I = KMnO_4 solution required for titration of the sample of raw soil, ml; and
J = KMnO_4 solution required for titration of the sample of soil-cement mixture ml.