

A Rapid Method for Determination of Cement Content of Cement-Treated Base Materials

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Evidence is presented to indicate that an EDTA titration under controlled conditions offers improved precision and accuracy over the presently accepted California method for the determination of the cement content of cement-treated base materials. Exclusive of sample preparation time, the new method permits a complete determination in 10 min or less as opposed to 1 hr or more for the California method. The new procedure uses ammonium chloride for the solvent system, the disodium salt of EDTA as titrant, and hydroxynaphthol blue as indicator.

•THE INCREASING USE of portland cement for the treatment of plastic-base materials has emphasized the need for developing a quick and moderately accurate method for determining the cement content of such materials. Accordingly, a study was initiated by the Nevada Department of Highways during the winter of 1963.

Curtis and Forbes (1) discussed and evaluated six methods for determining the cement content of treated base materials. They concluded that the California (2) and the conductivity methods (3) were the most practical for field use. For laboratory use they recommend the ASTM (4), the Versene (5, 6), or the California methods. The time required for a complete determination by the methods considered varied from 1 to 8½ hr. With present construction equipment having a capacity of 500 tons/hr or more, the time required for testing becomes extremely critical.

In an effort to decrease substantially the required testing time, the Materials and Research Laboratory of the Nevada Department of Highways studied possible modifications of the EDTA method for the determination of calcium for use as an index of the cement content of such materials.

PRELIMINARY

The analytical use of EDTA (ethylenedinitrilotetraacetic acid) and its disodium salt as reagents for the titrimetric determination of polyvalent cations through the formation of strong 1:1 complexes has been well established (7; 8, pp. 847-862). One of the chief disadvantages in the use of these methods has been the lack of specificity or selectivity of the available indicators. In 1963, a highly specific indicator for calcium was introduced, i. e., hydroxynaphthol blue (Mallinckrodt Chemical Works, Code No. 5630).

Preliminary experiments were performed using this new indicator and various solvent mixtures to find a combination that would permit either direct titration or titration of an aliquot of a sample solution. The method finally adopted (Appendix) was chosen for its simplicity, adaptability to field use, and accuracy, as well as for the ready availability and low cost of reagents.

Early experiments indicated that the use of the common laboratory acids, either singly or in combination, would be unsatisfactory due to the necessity of using heat or filtration subsequent to solution. Organic solvents were tried and discarded as either being too costly for volume work or too difficult to handle safely in the field. The solubility of calcium compounds in solutions of ammonium salts (9) was then exploited to develop the method as finally adopted. Ammonium chloride was chosen because of cost, availability, and ease of use in laboratory or field.

EXPERIMENTAL

Principle

The calcium compounds present in cement-treated base materials are taken into solution with ammonium chloride. An aliquot is removed from the resulting suspension and titrated with the disodium salt of EDTA after adjusting the pH between 13 and 13.5 to precipitate interfering substances such as iron, magnesium or aluminum. Cement content is determined from a standard curve after subtracting a blank for the calcium present in the aggregate.

TABLE 1
COMPARISON OF CALIFORNIA AND EDTA METHODS, 2 PERCENT CEMENT ADDED^a

Sample No.	California Method					EDTA Method					Operator
	Cement Found	d	d ²	p	p ²	Cement Found	d	d ²	p	p ²	
1	2.07	7	49	3.5	12.25	2.00	0	0	0	0	BR
2	2.00	0	0	0	0	1.95	5	25	2.5	6.25	BR
3	1.85	15	225	7.5	56.25	2.00	0	0	0	0	BR
4	2.11	11	121	5.5	30.25	2.00	0	0	0	0	BR
5	2.05	5	25	2.5	6.25	2.02	2	4	1.0	1.0	BR
6	2.17	17	289	8.5	72.25	2.01	1	1	0.5	0.25	PC
7	2.13	13	169	6.5	42.25	2.00	0	0	0	0	PC
8	2.05	5	25	2.5	6.25	2.00	0	0	0	0	PC
9	2.02	2	4	1.0	1.0	1.98	2	4	1.0	1.0	PC
10	1.87	13	169	6.5	42.25	2.01	1	1	0.5	0.25	RM
11	2.04	4	16	2.0	4.0	1.95	5	25	2.5	6.25	RM
12	2.08	8	64	4.0	16.0	1.93	7	49	3.5	12.25	RM
13	1.92	8	64	4.0	16.0	1.98	2	4	1.0	1.0	RM
14	1.95	5	25	2.5	6.25	2.05	5	25	2.5	6.25	JC
15	1.85	15	225	7.5	56.25	2.00	0	0	0	0	JC

^aCalifornia method: $s = 7.0$, $CV = 3.5$; EDTA method: $s = 2.1$, $CV = 1.1$.

TABLE 2
COMPARISON OF CALIFORNIA AND EDTA METHODS, 3 PERCENT CEMENT ADDED^a

Sample No.	California Method					EDTA Method					Operator
	Cement Found	d	d ²	p	p ²	Cement Found	d	d ²	p	p ²	
16	3.15	15	225	5.0	25.0	2.98	2	4	0.66	0.44	BR
17	3.07	7	49	2.3	5.29	3.00	0	0	0	0	BR
18	2.95	5	25	1.7	2.89	2.98	2	4	0.66	0.44	BR
19	3.00	0	0	0	0	2.98	2	4	0.66	0.44	BR
20	3.12	12	144	4.0	16.0	3.05	5	25	1.66	2.75	BR
21	3.17	17	289	5.7	32.49	2.98	2	4	0.66	0.44	PC
22	3.28	28	784	9.3	86.49	3.00	0	0	0	0	PC
23	3.50	50	2500	17.0	289.0	3.02	2	4	0.66	0.44	PC
24	3.14	14	196	4.7	22.09	3.00	0	0	0	0	PC
25	2.85	15	225	5.0	25.0	2.95	5	25	1.66	2.75	RM
26	3.00	0	0	0	0	3.05	5	25	1.66	2.75	RM
27	2.95	5	25	1.7	2.89	3.00	0	0	0	0	RM
28	3.08	8	64	2.7	7.29	3.02	2	4	0.66	0.44	RM
29	2.78	22	484	7.3	53.29	2.00	0	0	0	0	JC
30	2.78	22	484	7.3	53.29	3.05	5	25	1.66	2.75	JC

^aCalifornia method: $s = 13.5$, $CV = 4.5$; EDTA method: $s = 2.0$, $CV = 0.67$.

Procedure

Following the preliminary survey and determination of optimum conditions, an experiment was designed comparing the California and the EDTA methods at four different cement concentrations, keeping moisture, aggregate, and type of cement constant; operators were varied at each concentration level of cement. A supply of aggregate was obtained from a contract pit that would be used for actual construction. The aggregate was thoroughly blended and weighed into 120 portions. Cement was added in the amounts indicated in Tables 1 through 4. After thorough dry mixing, water was added to a moisture content of 8 percent, and the cement content was determined by both methods. Test results, estimated standard deviation, and coefficient of variation are as indicated in the tables.

DISCUSSION

As may be determined from the tables, the estimated standard deviation (s) and the coefficient of variation (CV) are substantially lower for the EDTA method than for the California method. Other than relative experience in laboratory technique, there seems to be no noticeable operator bias.

TABLE 3
COMPARISON OF CALIFORNIA AND EDTA METHODS, 4 PERCENT CEMENT ADDED^a

Sample No.	California Method					EDTA Method					Operator
	Cement Found	d	d ²	p	p ²	Cement Found	d	d ²	p	p ²	
31	4.12	12	144	3.0	9.0	4.03	3	9	0.75	0.56	BR
32	4.18	18	324	4.5	20.25	4.00	0	0	0	0	BR
33	4.05	5	25	1.25	1.56	4.00	00	0	00	0	BR
34	4.13	13	169	3.25	10.56	4.00	0	0	0	0	BR
35	4.07	7	49	1.75	3.06	4.02	2	4	0.50	0.25	BR
36	4.18	18	324	4.50	20.25	4.02	2	4	0.50	0.25	PC
37	4.30	30	900	7.50	56.25	4.00	0	0	0	0	PC
38	4.07	7	49	1.75	3.06	4.05	5	25	1.25	1.56	PC
39	4.17	17	289	4.25	18.06	4.00	0	0	0	0	PC
40	4.05	5	25	1.25	1.56	4.02	2	4	0.50	0.25	RM
41	4.04	4	16	1.00	1.00	3.98	2	4	0.50	0.25	RM
42	3.92	8	64	2.00	4.00	4.00	0	0	0	0	RM
43	3.84	16	256	4.00	16.00	4.00	0	0	001	0	RM
44	3.95	5	25	1.25	1.56	3.99	1	1	0.25	0.63	JC
45	3.97	3	9	0.75	0.56	4.00	0	0	0	0	JC

^aCalifornia method: $s = 9.4$, $CV = 2.36$; EDTA method: $s = 1.3$, $CV = 0.35$.

TABLE 4
COMPARISON OF CALIFORNIA AND EDTA METHODS, 5 PERCENT CEMENT ADDED^a

Sample No.	California Method					EDTA Method					Operator
	Cement Found	d	d ²	p	p ²	Cement Found	d	d ²	p	p ²	
46	5.13	13	169	2.60	6.76	5.00	0	0	0	0	BR
47	5.25	25	625	5.00	25.00	5.05	5	25	1.0	1.0	BR
48	5.18	18	324	3.60	12.96	5.00	0	0	0	0	BR
49	5.23	23	529	4.60	21.16	5.00	0	0	0	0	BR
50	5.12	12	144	2.40	5.76	5.05	5	25	1.0	1.0	BR
51	5.28	28	784	5.60	31.36	5.00	0	0	0	0	PC
52	5.19	19	361	3.80	14.44	5.00	0	0	0	0	PC
53	5.40	40	1600	8.00	64.00	5.10	10	100	2.0	4.0	PC
54	5.20	20	400	4.00	16.00	5.05	5	25	1.0	1.0	PC
55	5.08	8	64	1.60	2.56	4.95	5	25	1.0	1.0	RM
56	5.03	3	9	0.60	0.36	4.98	2	4	0.4	0.16	RM
57	4.98	2	4	0.40	0.16	5.01	1	1	0.2	0.04	RM
58	5.05	5	25	1.00	1.00	5.00	0	0	0	0	RM
59	5.00	0	0	0	0	4.95	5	25	1.0	1.0	JC
60	5.20	20	400	4.00	16.00	4.97	3	9	0.6	0.36	JC

^aCalifornia method: $s = 13.5$, $CV = 2.69$; EDTA method: $s = 2.8$, $CV = 0.56$.

Under normal experimental conditions, it was found desirable to add 20 percent triethanolamine solution as an additional precaution against interfering cations. As of the date of writing, more than 1,000 determinations have been made in the field with no difficulties encountered. The figures obtained by titration agree to 1 part in 100 with the theoretical amounts from plant operation; i.e., cement consumption, water usage, aggregate consumption, and truck weights.

As only a 10-ml aliquot is used for the titration, minor variations in moisture and calcium contents of the cement are of small moment. It is important to run blanks frequently, however. In actual field use, the calcium content of mixing water and aggregate can vary rather widely. Under the conditions existing in Nevada, the maximum daily variation in blank has been of the order of 1 ml EDTA. With the reagent strength we are using, this is the equivalent of 0.3 percent in the cement content. The most effective procedure we have been able to devise is that of belt sampling the aggregate immediately before sampling the cement-treated material and then running the two determinations simultaneously. This procedure, however, has been necessary on only one contract. On three other contracts, the blank never varied more than 0.1 ml, thus necessitating only one blank determination per day.

Experience has shown that time is a critical factor in the use of this procedure. With low cement contents and aggregate containing small amounts of calcium compounds, a stirring time of 1 min and a settling time of 3 min is quite satisfactory. With increasing cement content and/or greater amounts of calcium compounds present, it is necessary to increase the stirring time to 2 or 3 min and the settling time to 6 or 7 min. In no instance has a hydration period in excess of 10 min been necessary. Our experience has been limited to Nevada aggregates; accordingly, it may be necessary or desirable to experiment with the time factor in dealing with aggregates in different parts of the country.

Adding calcium compounds (e.g., oxide, carbonate, and sulfate) to aggregate blank and cement-treated material caused no difficulty, since the added material was compensated for in the blank determination.

By increasing hydration time, the method has been found applicable to materials up to 6 months old.

The method has not been applied to lime-stabilized materials, but theory indicates that it should apply equally well. It has been used with fresh and hardened concrete by changing the concentration of EDTA to 0.5 M. The main difficulty in dealing with wet concrete lies in obtaining a true sample. The extra moisture is readily compensated for by simple calculation.

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Appendix

DETERMINATION OF CEMENT CONTENT OF CEMENT-TREATED BASE MATERIALS

Principle

A 10 percent ammonium chloride solution is used as the solvent system for the calcium compounds present in cement-treated base materials. The solution is titrated with the disodium salt of EDTA (ethylenedinitrilotetraacetic acid) after adjustment of pH, using hydroxynaphthol blue as indicator. Cement content is determined from a standard graph after subtracting the aggregate blank.

Equipment for Field Use

- 6 - 10-ml volumetric pipettes;
- 2 - 25-ml burettes;
- 1 - Magnetic stirrer and stirring bar;
- 1 - Burette stand;
- 6 - 250-ml Erlenmeyer flasks;
- 6 - 2-qt polyethylene jugs;
- 6 - Stainless steel stirring rods (12 to 14 in.);
- 1 - Harvard trip balance with tared pan;
- 1 - 25-ml graduated cylinder;
- 1 - 1,000-ml graduated cylinder;
- 1 - Plastic funnel (12 in. diam.);
- 2 - 5-gal polyethylene jugs for distilled water;
- 1 - 5-gal polyethylene jug for ammonium chloride;
- 6 - Medicine droppers; and
- 1 - Pkg. pH indicator paper, range 10 to 14.

Reagents

1. EDTA, 0.1 M—Weight 116.88 g of EDTA (acid), A.C.S. Reagent grade, into a 3-l beaker. Add approximately 1.5 l of distilled water and place on stirrer. Add sodium hydroxide pellet by pellet until the acid is completely dissolved. Make up to exactly 4 l and transfer to a 1-gal polyethylene bottle. This solution must be stored in plastic. (For field use this solution will be made up and distributed by Headquarters Laboratory.)

2. Ammonium chloride solution, 10 percent—Transfer 1,893 g of U.S.P. granular ammonium chloride to a 5-gal plastic bottle. Make up to 5 gal with distilled water with thorough mixing.

3. Sodium Hydroxide, 50 percent—Dissolve 500 g of sodium hydroxide pellets in distilled water and dilute to 1 l. Use caution; store in plastic when cool. Dilute 1:1 with distilled water for use.

4. Triethanolamine, 20 percent—Dilute 100 ml of triethanolamine to 500 ml with distilled water.
5. Hydroxynaphthol blue—Obtain from Headquarters.

Caution

All equipment must be kept scrupulously clean and thoroughly rinsed with distilled water. All reagents must be stored in polyethylene containers.

Procedure

Preparation of Curve.—Prepare three duplicate samples as follows:

Set 1. Transfer two 300-gm samples of aggregate at the planned moisture content for the job to separate plastic containers. (The water used in bringing up the moisture to the correct amount should be that used at the job site.)

Set 2. Prepare two samples containing 2.5 percent cement of the type to be used on the job.

Set 3. Prepare two samples containing 5.0 percent cement.

Proceed with each sample as with production samples. Construct a graph showing milliliters EDTA vs percent cement (Fig. 1) using the average figures from Sets 1, 2 and 3. This should yield a straight line. Set 1 corresponds to the blank for the aggregate being used. If the aggregate blank changes, appropriate corrections must be made.

Production Samples.—Weigh into a 2-qt plastic container exactly 300 g of cement-treated material. Add 600 ml ammonium chloride solution and stir exactly 2 min with a stainless steel stirring rod. Allow to settle exactly 4 min and then pipette a 10-ml aliquot of the supernatant solution into a 250 ml Erlenmeyer flask. Add approximately 75 ml distilled water and with thorough mixing add the diluted NaOH dropwise until a pH between 13.0 and 13.5 is obtained using the pH indicator paper. Add 4 drops 20 percent triethanolamine solution and then add hydroxynaphthol blue indicator. Titrate with EDTA to a pure blue endpoint. Determine cement content from the previously prepared graph (Fig. 1).

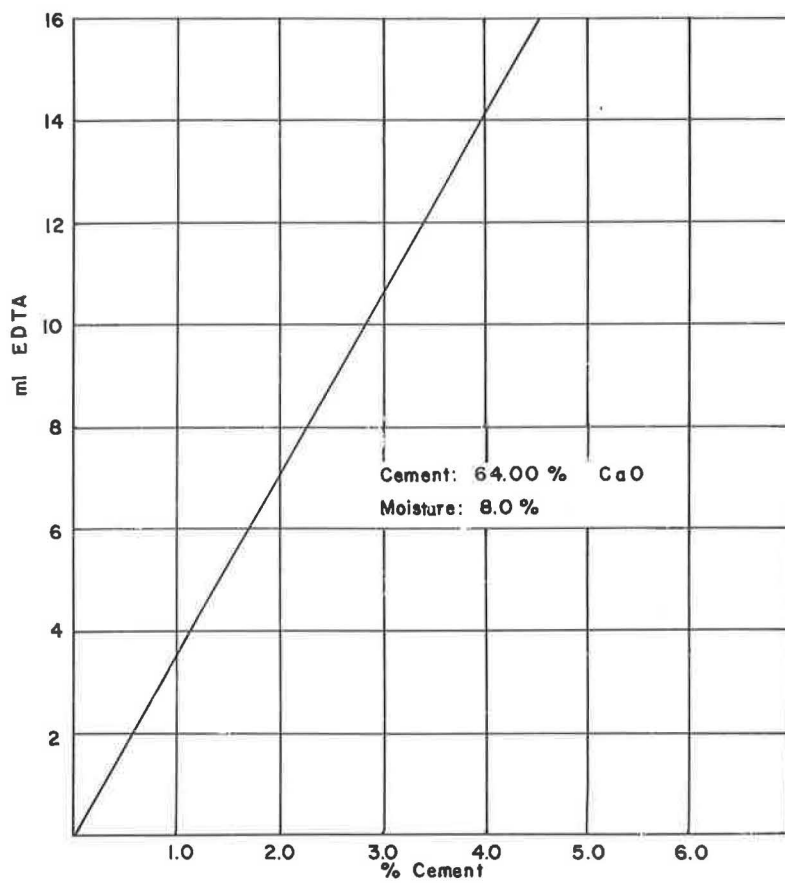


Figure 1.