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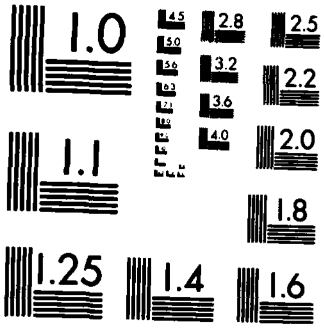

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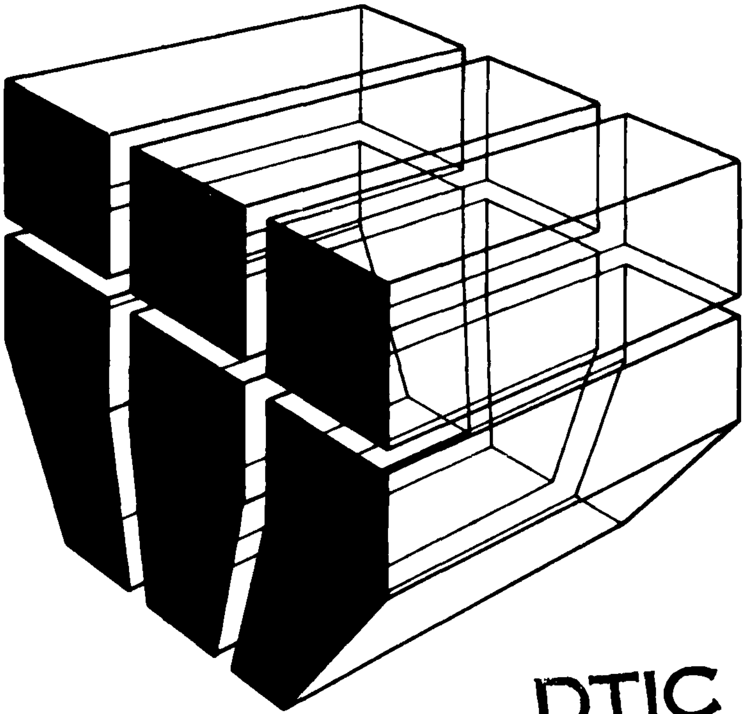
CERL

TECHNICAL REPORT M-85/08
DECEMBER 1984
Advanced Concepts for Quality Assurance

DEVELOPMENT AND EVALUATION OF A PROCEDURE FOR THE RAPID ANALYSIS OF FRESH CONCRETE



by
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This report presents the results of a study to develop and evaluate a procedure for the rapid determination of the cement and water contents of fresh concrete. Three generations of the procedure were considered:

Generation I: the original Kelly-Vail (KV) method developed by R. T. Kelly and J. W. Vail of the Greater London Council.

BLOCK 20. (Cont'd)

Generation II: the CERL/KV method, developed by the U.S. Army Construction Engineering Research Laboratory (CERL).

Generation III: the Corps of Engineers Concrete Quality Monitor (CE/CQM), also developed by CERL.

The abilities of Generation II and III methods to help predict cement and water contents of a variety of concrete mixtures were determined in an extensive series of side-by-side laboratory tests. The tests evaluated the effects of sampling techniques and aggregate type. Variance techniques were analyzed to help establish accuracy statements and to compare the two methods and the utility of these methods as bases for predicting concrete compressive and flexure strength was assessed. Also, field and additional laboratory tests of the Generation III method were conducted to determine (1) how the Generation III method performed under field conditions and (2) the effects of selected common admixtures on the output of the chloride meter used in the Generation III method.

The results demonstrated that the accuracies of Generations II and III (the CERL/KV and CE/CQM methods, respectively) were equivalent for identical test conditions and that aggregate characteristics affect the results of both cement content tests and both water content tests. It was also determined that actual water/cement ratios and water/cement ratios predicted on the bases of these methods may be used with equal accuracy for estimating 28-day concrete strength.

FOREWORD

This investigation was conducted for the Directorate of Engineering and Construction, Office, Chief of Engineers (OCE), under Project 4A162731AT41, "Military Facilities Engineering Technology"; Technical Area B, "Construction Management and Technology"; Work Unit 029, "Advanced Concepts for Quality Assurance." The Technical Monitor was Mr. Don Samanie, DAEN-ECC-C.

The study was performed by the Civil Engineering Department, West Virginia University (WVU), for the U.S. Army Construction Engineering Research Laboratory (CERL), under provisions in the modified CERL Contract No. DACA88-80-C-0017.

WVU personnel performing the study were Dr. W. J. Head and Mr. H. M. Phillipi. CERL personnel involved in the project were Paul A. Howdyshell and Debbie Lawrence of the Engineering and Materials (EM) Division. Dr. R. Quattrone is Chief of CERL-EM.

COL Paul J. Theuer is Commander and Director of CERL, and Dr. L. R. Shaffer is Technical Director.

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1 INTRODUCTION

Background

A method for determining the cement and water contents of freshly mixed Portland cement concrete was first suggested by Chaplin and Kelly in 1967 and described in detail by Kelly and Vail in 1968.[1] Subsequently, the U.S. Army Construction Engineering Research Laboratory (CERL) extensively tested and evaluated these methods. CERL demonstrated that the method is rapid, reliable, accurate, and usable under field conditions. It has since been proposed as an American Society for Testing and Materials (ASTM) standard test method.

CERL incorporated many new or revised testing procedures and equipment modifications into the original Kelly-Vail (KV) method. CERL's Generation I, the original KV method, is considered obsolete because the equipment is fragile and relatively difficult to operate under field conditions. Both Generations II and III of the method are essentially products of programs conducted by CERL researchers. Generation II, the CERL/KV method, is a useful, accurate, and verified system which has been used for rapidly analyzing fresh concrete in the field. Generation III, the recently developed Corps of Engineers Concrete Quality Monitor (CE/CQM) incorporates equipment which simplifies test procedures.

Objectives

The overall objectives of this study were to compare Generation II with Generation III and to make recommendations regarding the operation of Generation III equipment. Specific objectives were:

1. To evaluate the accuracy of Generations II and III in a series of side-by-side laboratory tests. Included was an assessment of the effects of coarse aggregate type on the methods' accuracy.

2. To compare the accuracy of Generation II with that of Generation III.

3. To recommend and assess changes in the test procedures of Generations II and III.

4. To develop correlations between predicted water/cement (w/c) ratios of concrete cylinder and beam samples and 28-day compressive and flexure strengths, respectively.

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[1] C. A. Chaplin and R. T. Kelly, "The Analysis of Concrete," Chemistry and Industry (September 2, 1967), pp 1467-1473; and R. T. Kelly and J. W. Vail, "Rapid Analysis of Fresh Concrete," Concrete (April and May 1968), pp 140-146 and 206-210.

5. To test Generation III under actual field conditions. Included was an assessment of the effects of selected common concrete admixtures on the output of the chloride meter used in the Generation III method.

Approach

A laboratory-based research program was conducted to evaluate and compare how accurately Generations II and III predicted the cement and water contents of selected fresh concrete mixtures. In addition, the ease of operation of Generation II and III equipment was assessed and concrete strength relationships were developed.

The program involved several test series in which aggregate type, mixture slump, and w/c mixture ratio were the variables. It was assumed that neither mixture slump nor w/c ratio affect the methods' accuracy; i.e., they were assumed to be accurate and reliable over the normal ranges of slump and w/c ratios encountered in the field. For each test series, enough concrete was mixed so:

1. Both a Generation II and III test for contents could be run.

2. Two 6-in. (152-mm) diameter x 12-in. (305-mm) high cylindrical specimens could be molded.

3. One 6 x 6 x 22 in. (152 x 152 x 559 mm) prismatic beam specimen could be prepared for the 28-day strength test.

The evaluations of the predicted cement and water contents were based on the percentage recovery (defined as 100 times the predicted value divided by the actual value) and the difference between the predicted and actual values. An analysis of variance techniques was used to compare methods and procedures. Ease of equipment operation was assessed as the program progressed; several modifications were suggested and subsequently incorporated. The observed strengths of the concrete samples were correlated with predicted w/c ratios.

For the Generation III field test, three concrete manufacturers of highway paving and bridge deck concrete were visited and the method tested at either the production facility or the job site. For the laboratory assessment of the effects of selected common admixtures on the output of the chloride meter, six 2-kg samples of concrete prepared identically except for admixture content were tested.

Mode of Technology Transfer

It is recommended that the results of this study be used to update the Corps of Engineers Handbook for Cement and Concrete; the methods discussed here also have potential for adaptation as an American Society for Testing and Materials (ASTM) standard test method.

2 OVERVIEW

Historical Review

Concrete technologists often design or proportion concrete mixtures based on both their past experience and assessments of trial mixes prepared in the laboratory or field. The goal of the mix design process, and indeed of all operations involved in concrete production, is an economical, usable product.

Concrete characteristics are greatly affected by how much water and cement are present in the mixture. Consequently, it is critical to select an appropriate w/c ratio for the mix design. Maintaining proper and consistent quantities of water and cement in the mixture is a major concern in subsequent batching operations. Distressed hardened concrete is often the result of too much water and not enough cement in the mix.

The goal of developing a rapid analysis method for determining the water and cement contents of fresh concrete is concrete quality control and quality assurance. A reliable method would provide direct and rapid verification of the amounts of ingredients actually present in a concrete mix.

Table 1 lists available rapid analysis methods* It should be noted that the term "rapid" is used in a relative sense. Certain methods require a few minutes to yield a result while other methods require 1 hour or more. Only one of the methods listed in Table 1 has been verified extensively in the field and can determine both the cement and water content of fresh concrete within 20 minutes: the KV method. (Statements about the KV method in Table 1 refer only to Generations I and II.)

Descriptions of Generations I, II, and III

Generations I, II, and III use the cement and water tests described below. However, the techniques, equipment, and analyses involved in estimating cement and water contents vary with each generation.

The cement content test involves separating a sample of a known mass of freshly mixed concrete over a nest of sieves wih a constant volume of water circulated in a domestic washing machine or fabricated suspension tank. Agitation serves to suspend the cement washed from the aggregate in the circulating water. A representative sample of a known volume of the cement-water mixture is obtained and mixed with a known volume of dilute nitric acid. The mixture of cement, water, and nitric acid is then agitated without heat to dissolve the calcium in the cement. The concentration of the dissolved calcium in the solution is determined and related to the cement content of the sample with the aid of a previously developed calibration curve.

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*Detailed descriptions of the operating principles, calibration requirements, test procedures, time requirements, error sources, accuracy statements, and estimated equipment cost for the methods listed in Table 1 can be found in W. J. Head and H. M. Phillippi, State of Technology for Quality Assurance of Plastic Concrete: Phase I -- Feasibility Study, Report No. FHWA/WV-80/006 (West Virginia Department of Highways, June 1980).

Table 1

Methods for Determining the Cement and Water Content of Fresh Concrete

			Method Appropriate for			
Method	Proposed and/or Developed by	Approximate Date of Development	Cement Content	Water Content	Basis of Method	Advantages of Method
Nuclear Cement Content Gage	Federal Highway Administration	1973	Yes	No	Nuclear (gamma ray backscatter and absorption)	1. Simple test procedure 2. Sample unaltered by test
Rapid Analysis Machine (RAM)	Cement and Concrete Association of Great Britain	1974	Yes	No	Mechanical (flocculation)	1. Simple test procedure 2. Fully automatic equipment 3. Rugged equipment
CERL/KV	Kelly and Vail; P. A. Howdyshell	Kelly/Vail in 1968 P. A. Howdyshell in 1974	Yes	Yes	Mechnical and chemical 1. Chloride ion titration for water content 2. Calcium titration for cement content	1. Determines both water and cement content 2. Compact equipment suitable for field use 3. Insensitive to aggregate moixture and mix proportions
Microwave Oven	North Dakota State Highway Department	1978	No	Yes	Microwave absorption	1. Simple test procedure 2. Test does not require constant operator attention
Constant Neutralization Method	California Department of Transportation	1976	Yes	No	Mechanical and chemical	1. Little equipment required fr test 2. Multiple samples can be tested simultaneously 3. Low cost
Hime and Willis	Hime and Willis	1955	Yes	No	Mechanical (heavy liquid separation)	1. Simple test procedure 2. Low cost
Hydrometer Analysis	L. J. Murdock	1948	Yes	No	Mechanical	1. Simple test procedure 2. Low cost

Table 1 (Cont'd)

Method	Proposed and/or Developed by	Approximate Date of Development	Method Appropriate for: Cement Content	Method Appropriate for: Water Content	Basis of Method	Advantages of Method
Dunagan Method	Dunagan	1933	Yes	Yes	Mechanical and buoyancy (wet-sieving process)	1. Will also determine aggregate/cement ratio and fine/coarse aggregate ratio 2. Fairly rugged equipment 3. Easy to set up in field 4. Easy to operate 5. Low cost
Consistency Predictions	S. Popovics	1966	Yes	Yes	Mechanical and physical 1. Penetration test 2. Slump test 3. Flow test 4. Remolding test	1. Employs standard field test 2. Simple test procedures 3. Low cost
S. G. Concrete Mix Tester	U.S. Naval Civil Engineering Laboratory	1961	Water/cement ratio only		Electrical resistance	1. Very rapid procedure 2. W/c ratio can be verified while the concrete is still in the mixer 3. Low cost
Conducti-metric Method	L. R. Chadda	1955	Yes	No	Electrical and conductivity	1. Simple procedure 2. Low cost
Absorption Method	L. R. Chadda	1955	Yes	No	Mechanical and chemical	1. Simple procedure 2. Low cost

Table 1 (Cont'd)

Method	Disadvantages of Method	Results Affected by	Reported Accuracy	Time Required for Analysis	Equipment Required	Equipment Commercially Available?
Nuclear Gage	1. Calibration curve required 2. Aggregate source and mix proportions should remain constant 3. Shipping regulations 4. License requirements	1. Chemical composition 2. Calcareous aggregates and other elements with atomic no. > 20 3. Dirty probe 4. Temperature	Cement content ±22 lb/cu yd* for certain siliceous aggregate mixes and ±31 lb/cu yd for calcareous aggregate	10-15 minutes	Nuclear cement content gage mixes	No
RAM	1. Calibration curve required 2. Aggregate source and mix proportions should remain constant 3. Unit weight 350 lb* 4. Operated on level floor 5. 110-volt AC supply required	1. Cement particles larger than 0.006 in. 2. Silt smaller than 0.006 in. 3. Entrained air	Cement content ±17-35 lb/cu yd	5-10 minutes	RAM device, scales, buckets, hydrochloric acid, flocculating agents	Yes, marketed by Wexham Developments (UK) and Soiltest, Inc. (USA)
CERL/KV	1. Calibration curve required 2. Fragile equipment 3. Requires AC current 4. Requires water supply	1. Calcareous aggregate; measures all calcium that passes the finest sieve (No. 50 or No. 100) 2. Perceptibility of end point reaction	Cement content within about ±28 lb/cu yd;** water content within about ±0.24 gal/sack**	15 minutes	Reagents scale, mixer beakers, pipettes, washing machine, sieves, burette, carboys	No, assembled from standard laboratory equipment
Microwave Oven	1. Must be tested within 1 hour after mixing 2. Total water content is determined 3. AC current required	1. Water lost to evaporation between mixing and start of test 2. Admixtures which act as an evaporative liquid 3. Melting of cement in oven 4. Aggregate absorption	Water content within ±0.06 gal/sack at 95% confidence level or ±0.08 gal/sack at 99% confidence level	About 60 minutes	Microwave oven, scales, containers, scoops	Yes, microwave oven must include defrost mode

*Metric conversions: 1 gal = 0.0038 m^3; 1 in. = 0.0254 m; 1 lb = 4.45 N; 1 lb/cu yd = 5.82 N/m^3; 1 gal/sack = 9100 mm^3/N.

**Representative value estimated for typical mixes based on reported method accuracy.

Table 1 (Cont'd)

Method	Disadvantages of Method	Results Affected by	Reported Accuracy	Time Required for Analysis	Equipment Required	Equipment Commercially Available?
Constant Neutralization	1. Calibration curve required 2. Cement and aggregate source should remain constant 3. Operator must maintain a neutral solution by adding acid at 1 minute intervals for 1 hour	1. Excess acid attacking aggregates 2. Calcareous aggregates	Cement content within about 24 lb/cu yd*	90 minutes	Scale, No. 4 sieve, titrating burette, burette stand & clamp, eye dropper, stirring rods, containers, timer	No, assembled from standard laboratory equipment
Hime and Willis	1. Calibration curve required 2. Cement source should remain constant 3. Lengthy test period (more than 1 hour) 4. Significant operator judgment required	1. Specific surface area of cement 2. Specific gravity of separating media 3. Centrifugal forces acting on tube (volume) 4. Incomplete separation	Average error with Type I cement was 13 lb/cu yd with a standard deviation of 20 lb/cu yd. Average error with Type III cement was 21 lb/cu yd with a standard deviation of 27 lb/cu yd	75 minutes	Scale, No. 300 sieve, pans, brush, burners, centrifuge and tubes, tachometer, flocculating agent	No, assembled from standard laboratory equipment
Hydrometer Anaysis	1. Calibration curve required 2. Fragile equipment 3. Stable platform required for hydrometer readings 4. Operator judgment required	1. Silt passing No. 100 sieve 2. Fineness of cement 3. Temperature 4. Cement retained on No. 100 sieve	Cement content within about 22 lbs/cu yd**	About 30 minutes	Scale, sieves, metal container, paddle, scoops, hydrometer, graph paper	No, assembled from standard laboratory equipment
Dunagan Method	1. Specific gravity of aggregates assumed constant 2. Operator must judge surface-dry conditions 3. Aggregate source should remain constant	1. Cement retained on No. 100 sieve 2. Silt passing No. 100 3. Variation in specific gravity of aggregates 4. Grinding action of mixer	Cement content within about ±38 lb/cu yd**; water ±1.5 gal/sack**	10-20 minutes	Scale, sieves, containers	No, assembled from standard laboratory equipment

Table 1 (Cont'd)

Method	Disadvantages of Method	Results Affected by	Reported Accuracy	Time Required for Analysis	Equipment Required	Equipment Commercially Available?
Consistency Predictions	Questionable accuracy	1. Maximum particle size 2. Type of cement 3. Mixing time 4. Temperature 5. Admixtures	Not reported, but the results are very unreliable	Time required for two consistency tests	Slump cone, flow table, penetration plunger and mold	No, assembled from standard laboratory equipment
S. G. Mix Tester	1. Must be calibrated 2. Aggregate source should remain constant 3. Can only verify the w/c ratio of a predetermined mix	1. Chemical composition 2. Alkali variations or the presence of chlorides and other metal ions 3. Admixtures 4. Dirty electrodes	Device detects only those changes greater than 0.03 in w/c ratio and readings are correct to the nearest 0.07 difference in w/c ratio	1 minute	S. G. Concrete Mix Tester	The U.S. Navy obtained the device through the Square Grip Reinforcement Company Limited (London). Current availability unknown.
Conductimetric Method	1. Calibration curve required 2. Accuracy not established 3. Conductivity could depend more on the water content than on the cement content	1. Alkali variation or the presence of chlorides and other metal ions 2. Admixtures 3. Temperature 4. Chemical composition	Not reported	Not reported	Scale, No. 100 sieve, buckets, scoops, beakers & lids, distilled water	No, assembled from standard laboratory equipment
Absorption Method	1. Calibration curve required 2. Aggregate moisture conditions should remain constant 3. Accuracy not established	1. Fineness of cement 2.. Temperature 3. Percent absorption of aggregates 4. Initial conditions of aggregate	Not reported	Not reported, estimated 30-60 minutes	Scale, No. 40 sieve buckets, scoops, beakers & lids,	No, assembled from standard laboratory equipment filters, titrating flask, potassium permanganate

The cement content test is based on the following assumptions:

1. Calcium compounds are uniformly distributed in the cement.

2. Cement can be dispersed in water and held in suspension so that a representative sample can be obtained.

3. A solution whose calcium concentration can be determined can be obtained by adding cement to nitric acid and stirring the mixture in the absence of external heat.

4. The calcium content of the solution can be determined with the aid of a flame photometer (Generation I), ethylenediaminetetra acetate dihydrate (EDTA) titration (Generation II), or a commercially available automatic calcium analyzer (Generation III).

The water content test involves mixing a sample of fresh concrete of a known mass with a salt solution (sodium chloride) of a prescribed concentration and volume. The chloride concentration of the intermixed solution is determined; the water content of the concrete sample is directly related to the difference in chloride concentrations between the original salt solution and the intermixed solution. The method is based on the premise that water in fresh concrete is available for intermixing with aqueous solutions. Thus, if an aqueous solution with a known concentration of chlorides and a known volume is added to a concrete sample and none of the solution is absorbed by the aggregates or cement, the volume of water in the sample can be determined by finding the concentration of chlorides in the intermixed solution. Symbolically:

$$B \times S_1 = (A + B)S_2 \qquad \text{[Eq 1]}$$

where:

B = volume of aqueous solution
S_1 = chloride concentration of aqueous solution
A = volume of water in the sample
S_2 = chloride concentration of the intermixed solution

If the volume of the aqueous solution and the chloride concentration of the aqueous solution are fixed and the chloride concentration of the intermixed solution is measured independently, then the volume of water in the sample can be calculated. Assuming that the water absorbed by the aggregates is not available for intermixing, the predicted water content should more closely represent the free-water content of the concrete mixture rather than the total-water content. (The free-water content is the difference between the total-water content and the water absorbed by the aggregates.) When the concrete sample contains chloride compounds from other sources, calibration tests must be performed on both a regular sample and a blank consisting only of distilled water.

Generation I

The Generation I method uses flame photometry (calcium signature) to determine cement content. A small quantity of the sample solution is transferred into a glass beaker, then offered to the inlet tube of the flame photometer. When a calcium solution is atomized and passes into the nonluminous flame of the photometer, the flame turns a characteristic brick-red color. The color varies in intensity with the concentration of calcium ions present. The photometer measures the intensity of the coloration; by comparing the intensity with that obtained from standard strength calcium solutions, the calcium content of a solution of unknown strength can be established and related to cement content through previously established calibration curves. The constant subdued-light requirement of the flame photometer means that, for field use, it must be placed either in a pickup truck camper or a small trailer.

The calibration curve used to determine cement content is established by performing a standard cement content test on both tap water and a cement solution. The cement solution used for calibration should be equivalent to a sample of concrete containing 24 percent cement by mass. The flame photometer reading obtained for the tap water represents 0 percent cement. The reading obtained for the cement solution represents a cement content of 24 percent. Because all unknown cement contents are linearly proportional to these two readings, a calibration curve can be easily constructed.

The Generation I water content test uses a volumetric chloride ion titration procedure. In this procedure, Volhard's method,[2] an excess of a standard solution of 0.5 N silver nitrate ($AgNO_3$) is added to 50 ml of the diluted 0.5 N sodium chloride solution (NaCl), thus precipitating silver chloride. The precipitate is then flocculated with nitrobenzene so the concentration of excess silver nitrate in the supernatent liquid can be determined by titration against 0.05 N potassium thiocyanate (KSCN). The water content can then be predicted by:

$$\text{Percent water} = \frac{50\ Z}{500 - Z} \qquad \text{[Eq 2]}^3$$

where:

$Z = Y' +$ volume in milliliters of potassium thiocyanate required to reach the end point of the sample.

$Y' = 100 - X$

$X =$ volume in milliliters of potassium thiocyanate required to reach the end point of the blank.

The end points are denoted by a significant color change in the test solution.

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[2] Arthur I. Vogel, A Text-Book of Quantitative Inorganic Analysis, Third Edition (Longmans, London 1968).

[3] P. A. Howdyshell, Revised Operations Guide for a Chemical Technique to Determine Water and Cement Content of Fresh Concrete, Technical Report (TR) M-212/ADA039120 (Construction Engineering Research Laboratory [CERL], April 1977).

Eq 2 is only valid when the silver nitrate: sodium chloride: potassium thiocyanate concentration ratio is 1:1:10. When the concentration ratios are not 1:1:10, the water content is by:

$$\text{Percent water} = 50\,\frac{1 - 0.8A - 2B + 0.02BZ}{0.8A + 2B - 0.02BZ} \qquad [\text{Eq } 3]^{4}$$

where:

A = silver nitrate normality/sodium chloride normality

B = potassium thiocyanate normality/sodium chloride normality

It is often necessary to check the strengths of the reagents by the Mohr method[5] of end point titration to ensure that the reagents have not deteriorated.

Generation II

In Generation II, the cement test is performed by titrating a sample with an EDTA solution in the presence of a buffer and an eriochrome black T indicator. A small quantity of the sample solution is transferred into a small glass beaker, where a buffer solution and a few drops of eriochrome black T indicator are added. This mixture is titrated with EDTA solution until the end point is reached (denoted by a significant change in the color of the mixture). The amount of EDTA used to reach the end point is noted and a previously prepared calibration curve for the particular cement is used to determine the amount of cement in the sample.

The calibration technique is the same as used for Generation I, except that a titration process is used instead of a flame photometer. The titration process eliminates the subdued-light requirement of the flame photometer test, increasing the system's versatility. During the development of Generation II, aggregate blanks were added to the calibration procedure. The results of the aggregate blank tests are subtracted from the results of the cement content test to account for calcium in the aggregate passing the finest sieve used to prepare the sample. The aggregate blanks are determined by performing a standard cement content test on aggregate samples. A separate calibration test is performed on each aggregate in the concrete. When both coarse and fine aggregate are silicious, the aggregate correction factors will be about zero. When a calcareous coarse aggregate is used with a silicious fine aggregate, the resulting coarse aggregate correction factor will probably be small. However, when calcareous fine aggregates are encountered, the correction factor will significantly affect the predicted value of cement content.

The Generation II water content test is the same as Generation I, except a 25-ml sample of the intermixed salt solution is used instead of a 50-ml sample. A different calibration technique is also used. The smaller sample

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[4] P. A. Howdyshell, TR M-212.
[5] Arthur I. Vogel.

size decreases the amount of silver nitrate needed per test, lowering the cost of each test. In light of field experience, it was recommended that an experimentally determined calibration curve be used to relate water content to the volume of potassium thiocyanate employed in the titration process.[6] This meant three blank water content tests had to be done. The blank water content tests were performed as standard water content tests, except known volumes of water were used instead of a concrete sample. Test results are plotted as three points on the water content vs potassium thiocyanate curve. The need to rebalance reagent strengths is eliminated because the experimental curve precludes the requirement that the reagent strengths be exactly in the ratio of 1:1:10. And since reagent strengths change with time, the experimental curve effectively bypasses the problems associated with reagent storage.

Generation III

In the Generation III method, a calcium analyzer and a chloride meter are used to determine calcium and chloride solution concentrations. (Appendix A describes the commercially available calcium analyzer and chloride meter.)

In the cement test, a small quantity of the sample solution is transferred from a pipet into the cuvette compartment of the calcium analyzer; the cuvette door is closed and the titrate button is pushed. The calcium concentration which appears on a digital display indicates the amount of cement in the solution. Previously established calibration curves are used to relate analyzer readings to cement contents.

The cement calibration method for Generation III differs from that used in Generations I and II. The amount of mixture ingredients is reduced proportionately to produce a 2-kg sample of concrete. Following mixing, the 2-kg sample is washed over the sieves into the washing machine or suspension tank. A cement content test is performed on the solution. The result represents one point on a calibration curve corresponding to the mass of cement in the sample. This procedure incorporates all sources of calcium and eliminates the need to test aggregates individually. A 2-kg blank sample consisting of all the materials and mix proportions of the concrete to be tested minus the cement represents zero cement. This sample allows even additives like flyash to be corrected for. For this study, a sample of tap water was tested instead of a 2-kg blank sample to establish the zero cement point on the calibration graph. This calibration process was used throughout the project reported here for both Generations II and III.

The calibration curve and many of the reagents used in Generations I and II are eliminated in the Generation III water content test. A sample of the intermixed salt solution is first centrifuged and the chloride concentration of the resulting supernatent liquid is determined by placing a prescribed volume of the liquid into the chloride meter beaker, lowering the electrodes into the liquid, and pushing the titrate button. The chloride concentration

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[6] A. J. Nauratil and P. A. Howdyshell, "CERL/KV Field Tests at Chief Joseph Dam," paper presented at the American Society for Testing and Materials (ASTM) Committee C9-9.03 Meeting, Philadelphia, PA (June 18, 1979).

appears on a digital display. The water content of the sample tested is found from:

$$A = B \left[\frac{S_1}{(S_2 - S_B)} - 1 \right] \qquad \text{[Eq 4]}$$

where:

A = volume of water in milliliters = mass of water in grams in the sample

B = initial volume of salt solution added to the sample

S_1 = chloride concentration of salt solution initially added to the sample

S_2 = chloride concentration of intermixed salt solution

S_B = chloride concentration of blank sample (distilled water is added to the blank).

Blank samples are tested when the concrete contains chlorides from other sources. Subsequently, blank test results (S_B) are subtracted from the sample test results (S_2).

Much of the fragile glassware associated with Generations I and II was eliminated in Generation III. Reagent costs were also significantly reduced. With the exception of a 5 percent nitric acid solution and a 0.5 N NaCl solution, all reagents can be purchased in small prepackaged containers from the equipment manufacturer.

Sample Size

Concrete samples of 1 kg were used in the Generation I tests. However, during CERL's field tests at the Chief Joseph Dam project, 2-kg samples were used to good effect, so it was recommended that the sample mass be increased to 2 kg.[7] This recommendation was based on test results which indicated that the accuracy of the Generation I method was enhanced by a larger test specimen. In addition, concrete strengths estimated based on the method's predicted w/c ratios were significantly more accurate when tests used the 2-kg specimens rather than the smaller specimens. Gaynor and Meininger[8] also suggested using 2-kg specimens, indicating it was difficult to obtain a representative sample of concrete when the sample mass was 1 kg. They also found that increasing the sample mass would increase the accuracy and lower the variability of test results.

The Generation II method was changed to incorporate 2-kg samples. Generation III was modified to incorporate 2 kg ± 200 gram samples. The purpose of the Generation III modification was to prevent operators from

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[7] A. J. Nauratil and P. A. Howdyshell.

[8] R. D. Gaynor and R. C. Meininger, "A Study of Sampling Procedures on Coarse Aggregate Content and Results of Kelly-Vail Tests for Cement Content of 1 Cubic Foot Concrete Batches (Series 208C)," paper presented at ASTM Committee C9-9.03 Meeting, Philadelphia, PA (June 19, 1979).

biasing the sample's mortar/aggregate ratio by adjusting the sample mass. Samples of 2 kg ± 200 grams mass were used throughout the project reported here. More detailed descriptions of the Generation II and III test procedures used throughout this project are given in Appendices B and C, respectively.

Assessments of Previous Research and Development

The accuracy and usefulness of the Generation I method in determining cement and water contents have been extensively investigated in the laboratory and field. Table 2 summarizes the results of many of those projects. All results in Table 2 pertain to Generations I and II. Very little research has been reported on the more recently developed Generation III. It is difficult to match the sources and results in Table 2 specifically with either Generation I or II as described in previous sections of this report, because changes in equipment and procedures evolved gradually. Also, the cement and water content tests were developed independently. Consequently, no well-defined demarcation exists between Generations I and II.

Results appearing in Table 2 were based on percentage recovery. All water content test results were determined based on free-water content. Research results to date generally indicate that water content test results more closely represent free-water than total-water contents. The values in Table 2 can serve as benchmarks for assessing the results of the present project.

Table 3 gives the results of Generation III tests and information on Generation II and III test results.[9] The test series performed Generation II and III cement and water tests on air- and nonair-entrained concrete samples. All concrete mixtures used a Type I Portland cement, siliceous river sand and a calcareous coarse aggregate. The mixtures were similar to the mixture used in the present project. Generation II and III water tests were performed on the same sample. Centrifuging was not employed to separate solids from the intermixed salt solution in the Generation II water test. A 20- µl sample was used in the Generation III water test to determine the chloride concentration of the intermixed salt solution.

Table 3 indicates little difference between the Generation II and III cement content tests. The Generation III water test results indicate a high mean percent recovery for air-entrained mixtures. This result was attributed to suspended solids which were not completely settled or removed from the 20-µl test sample. (Suspended solids in the test sample would result in low chloride concentrations and correspondingly high water content results.) It was also observed that suspended solids were present in greater amounts in tests of air-entrained concrete than in tests of nonair-entrained concrete because entraining agents tend to act as dispersents. This project concluded that Generation III water test samples should be centrifuged and suggested using a 100-µl instead of a 20-µl test sample.

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[9] P. A. Howdyshell, Corps of Engineers Concrete Quality Monitor: Operations Guide, TR M-293/ADA102753 (CERL, May 1981).

Table 2

Summary of Results of Previous Research/Development Projects Using Generations I and II

		Cement Content Test			Water Content Test*		
No.	References	Number of Samples Tested, n	Mean Percent Recovery, $\bar{X}$	Standard Deviation, S	Number of Samples Tested, n	Mean Percent Recovery, $\bar{X}$	Standard Deviation, S
1	A*	12	93.53	6.77	12	94.17	3.68
2	A	16	104.77	5.96	16	94.86	3.62
3	A	16	94.03	6.03	16	100.23	3.25
4	A	44	97.79	8.06	44	96.56	4.40
5	B	39	96.9	3.2	16	94.2	2.3
6	B	33	99.0	4.6	30	100.0	4.1
7	C	17	101.6	3.91	24	130.3	19.55
8	C	23	97.6	1.46	23	107.9	4.90
9	C	23	99.7	7.13	3	116.9	4.03
10	C	28	109.0	6.63	28	118.7	9.85
11	C	14	98.9	3.07	14	100.6	2.70
12	C	14	102.5	5.94	14	110.8	5.09
13	C	119	102.0	4.83	126	115.7	8.33
14	D	10	89.7	2.4	10	102.1	4.2
15	D	10	88.9	3.1	10	102.9	6.1
16	D	10	96.8	10.7	10	101.7	5.7
17	D	10	92.5	6.7	10	98.1	3.7
18	D	40	92.0	7.1	40	101.2	5.2
19	E	11	88.4	8.2	11	115.0	10.7
20	E	12	75.7	9.0	12	91.3	6.2
21	E	11	113.4	7.6	11	106.2	10.0
22	E	6	131.3	17.1	6	109.4	8.4
23	E	10	110.2	4.6	10	103.5	9.1
24	E	80	98.6	3.5	80	101.1	11.2
25	E	12	92.7	7.8	12	132.5	5.9
26	E	16	98.8	12.5	16	135.4	10.5
27	E	11	93.2	13.8	14	99.4	15.2
28	F	16	142	15.4	16	150	33.3
29	F	16	106	11.3	16	112	25.3
30	F	14	143	15.4	14	151	34.6
31	F	14	106	12.1	14	112	26.4
32	F	2	138	1.4	2	144	31.8
33	F	2	102	0.7	2	107	22.6
34	F	93	103	11.9	93	100	12.2
35	F	36	102	15.6	36	102	15.2
36	F	57	104	3.8	57	99	9.8
37	F	17	96	10.0	17	94	11.2
38	F	5	94	14.4	5	94	15.7
39	F	12	96	8.3	12	94	9.6
40	F	55	102	14.3	55	104	19.1
41	F	71	103	9.1	71	98	10.2
42	F	126	103	11.9	126	101	15.0

[A] P. A. Howdyshell, Laboratory Evaluation of a Chemical Technique to Determine Water and Cement Content of Fresh Concrete, Interim Report M-97/ADA784055 (CERL, July 1974).

[B] R. T. Kelly and P. J. Baldwin, "The Kelly-Vail Chemical Technique for Water and Cement Content," Rapid Testing of Fresh Concrete, Conference Proceedings M-128/ADA784055 (CERL, May 1975).

[C] P. A. Howdyshell, "Concrete Quality Control: 28 Days-24 Hours-15 Minutes," American Concrete Institute Journal, International Symposium on Accelerated Strength Testing, Mexico City (1976), pp 183-200.

[D] P. A. Howdyshell, "Determination of Water and Cement Content of Fresh Concrete by Nuclear and Chemical Methods," thesis presented to the University of Illinois, at Urbana-Champaign, IL (1977).

[E] H. D. Pritchett, "Report on the Field Evaluation Study for the Kelly-Vail Rapid Concrete Test Procedure," paper presented at the Annual Meeting of the Transportation Research Board, Washington, D.C. (January 18, 1978).

[F] A. J. Nauratil and P. A. Howdyshell, "CERL/KV Field Tests at Chief Joseph Dam," paper presented at ASTM Committee C9-9.03 meeting, Philadelphia, PA (June 18, 1979).

* Water content test results based on free-water content.

Table 3

Summary of Results of Previous Tests Using Generations II and II

Type of Concrete Tested		Generation II		Generation III	
		Cement	Water*	Cement	Water*
Nonair-Entrained	Number of Samples, n	39	38	39	39
	Mean Percent Recovery, $\bar{X}$	100.7	101.8	97.3	101.9
	Standard Deviation, S	5.7	6.8	5.4	5.9
Air-Entrained	Number of Samples Tested, n	24	24	24	24
	Mean Percent Recovery, $\bar{X}$	99.7	100.6	98.5	112.9
	Standard Deviation, S	5.8	10.9	4.8	7.6

*Water content test results based on free-water content

3 EXPERIMENTAL TEST SERIES

This chapter describes a series of experiments conducted to (1) see how quickly a technician could learn to work with Generation II and III equipment and (2) determine how certain procedures affect the reproducibility and accuracy of test results.

Table 4 lists the concrete mixture proportions used in this experimental series. It also lists the ingredient masses used to make the 2-kg test specimens. All samples were mixed with the same ingredient mass, except for the samples of air-entrained concrete, which had 1 ml of Daravair-R air-entraining admixture added to the mixing water. This volume of air-entraining admixture was equivalent to 4.35 fluid ounces per sack of cement.

Before mixing, the river sand fine aggregate was blended with enough water to bring the sand to slightly above the saturated-surface-dry (SSD) condition. The moist material was then stored in a sealed container. The crushed limestone coarse aggregate was soaked in water; subsequently, the free water was drained at least 1 hour before mixing. (Appendix D lists the aggregates' characteristics.) Samples of concrete were fabricated by weighing out the ingredients, placing them into a 2-qt (1.9-L) polyethylene container, and mixing in an end-over-end mixer for at least 5 minutes. In all cases, care was taken to produce identical samples of concrete.

Table 4

Proportions of Mixture Used in the Experimental Test Series

	Typical Weights of Ingredients Per Cubic Yard of Concrete* lb (kg)	Mass of Ingredients in 2-kg Samples (grams)
Cement	630 (285)	332.7
Water	315 (142)	166.0
Fine Aggregate	1175 (532)	620.7
Coarse Aggregate	1667 (528)	880.6
Total	3787 (1715)	2000.0

*Based on saturated-surface-dry (SSD) conditions

Cement Content Tests

Two series of cement content tests were conducted. Generation II equipment was used in one series, Generation III equipment in the other. For each series, 2-kg samples of concrete were prepared and washed over the No. 4 and No. 50 sieves into water in the cement suspension tank. Eight subsamples were then taken from the tank. Four subsamples were analyzed using the Generation II equipment; the remaining four were analyzed using Generation III equipment. Three cement content tests were performed on each subsample. The preparation, sampling, and testing process was repeated for all four samples. Two of the samples were air-entrained concrete, the other two were nonair-entrained concrete. Cement from samples of each type of concrete was also separated from the concrete in the domestic washing machine; the remaining two samples were processed in the fabricated circulating tank.

Tables 5 and 6 list the results of these experiments. Table 5 gives the EDTA volumes obtained using Generation II equipment, Table 6 the calcium analyzer readings obtained using Generation III equipment. The mean and variance for each subsample appear directly below the respective data; the overall mean and variance for each sample are shown at the bottoms of the tables. Percentage recovery was not calculated because the numbers appearing in each table can be compared directly. The same lot of reagents was used to make all determinations.

The ingredients and treatments of all samples were identical, except an air-entraining admixture was added and two cement suspension tanks were used. Consequently, constant experimental data were anticipated since the response variable was assumed to be affected only by calcium concentration. A nested analysis of variance (ANOVA) was conducted at $\alpha = 0.01$ level of significance to verify this assumption. The ANOVA model was:

$$y_{ijk} = \mu + \alpha_i + \beta_{ij} + \varepsilon_{ijk}; \ (\alpha_i \text{ fixed; } \beta_{ij} \text{ random}) \qquad \text{[Eq 5]}$$

where

y_{ijk} = the effect due to each individual observation

μ = the effect due to the overall mean

α_i = the effect due to each sample

β_{ij} = the effect due to each subsample

ε_{ijk} = the random effect containing all uncontrolled sources of variability due to sampling.

These ANOVA are listed in Table 7 and 8 for the EDTA volumes and the calcium analyzer readings, respectively. Cochran's test[10] for homogeneity of variances was used to help assess the ability of a technician to obtain reproducible data. Cochran's test was applied to both EDTA volume and the calcium analyzer data. Test results indicated that the variances for the respective subsamples were homogenous.

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[10] R. E. Walpole and R. H. Myers, Probability and Statistics for Engineers and Scientists, Second Edition (Macmillan Publishing Co., Inc., 1978).

Table 5

EDTA Volumes for Identical Samples and
Subsamples from Experimental Test Series
for the Generation II Cement Content Test

	Samples			
	Sample 1 Nonair-Entrained Domestic Washing Machine	Sample 2 Air-Entrained Domestic Washing Machine	Sample 3 Nonair-Entrained Fabricated Circulating Tank	Sample 4 Air-Entrained, Fabricated Circulating Tank
Subsamples 1	59.0 58.8 60.2 $\bar{X}$ = 59.3333 S^2= 0.5733	59.4 60.6 59.8 $\bar{X}$ = 59.9333 S^2= 0.3733	57.0 57.4 58.0 $\bar{X}$ = 57.4667 S^2= 0.2533	57.0 56.6 56.6 $\bar{X}$ = 56.7333 S^2= 0.0533
2	58.2 59.8 59.4 $\bar{X}$ = 59.1333 S^2= 0.6933	58.2 58.0 58.0 $\bar{X}$ = 58.0667 S^2= 0.0133	55.6 58.8 57.4 $\bar{X}$ = 57.2667 S^2= 2.5733	53.8 55.6 56.0 $\bar{X}$ = 55.1333 S^2= 1.3733
3	60.0 60.4 60.8 $\bar{X}$ = 60.4000 S^2= 0.1600	53.0 53.2 53.6 $\bar{X}$ = 53.2667 S^2= 0.0933	56.0 55.8 57.4 $\bar{X}$ = 56.4000 S^2= 0.76000	56.0 57.4 56.6 $\bar{X}$ = 56.6667 S^2= 0.4933
4	61.0 60.0 60.0 $\bar{X}$ = 60.3333 S^2= 0.3333	56.4 57.8 58.6 $\bar{X}$ = 57.6000 S^2= 1.2400	56.0 57.6 57.8 $\bar{X}$ = 57.1333 S^2= 0.9733	56.0 56.2 56.4 $\bar{X}$ = 56.2000 S^2 = 0.0400
	Overall Means and Variances for Each Sample			
	n=12 $\bar{X}$= 59.8000 S^2= 0.6764	n=12 $\bar{X}$= 57.2167 S^2= 6.8179	n=12 $\bar{X}$= 57.0667 S^2= 1.0061	n=12 $\bar{X}$= 56.1833 S^2= 0.8033

Table 6

Calcium Analyzer Readings for Identical Samples and Subsamples from Experimental Test Series for the Generation III Cement Content Test

		Samples			
		Sample 1 Nonair-Entrained, Domestic Washing Machine	Sample 2 Air-Entrained, Domestic Washing Machine	Sample 3 Nonair-Entrained, Fabricated Circulating Tank	Sample 4 Air-Entrained, Fabricated Circulating Tank
Subsamples	1	7.45 7.08 7.33 $\bar{X}$ = 7.2867 S^2= 0.0356	7.29 7.49 7.48 $\bar{X}$ = 7.4200 S^2= 0.0127	6.50 6.78 6.74 $\bar{X}$ = 6.6733 S^2= 0.0229	6.84 6.86 6.94 $\bar{X}$ = 6.8800 S^2= 0.0028
	2	7.36 7.41 7.40 $\bar{X}$ = 7.3900 S^2= 0.0007	7.55 7.47 7.65 $\bar{X}$ = 7.5567 S^2= 0.0081	6.89 6.93 6.97 $\bar{X}$ = 6.9300 S^2= 0.0016	7.09 6.98 6.89 $\bar{X}$ = 6.9867 S^2= 0.0100
	3	7.34 7.26 7.46 $\bar{X}$ = 7.3533 S^2= 0.0101	7.57 7.49 7.79 $\bar{X}$ = 7.6167 S^2= 0.0241	6.98 6.85 6.89 $\bar{X}$ = 6.9067 S^2= 0.0044	7.00 7.06 7.26 $\bar{X}$ = 7.1067 S^2= 0.0185
	4	7.38 7.44 7.31 $\bar{X}$ = 7.3767 S^2= 0.0042	7.61 7.68 7.40 $\bar{X}$ = 7.5633 S^2= 0.0212	7.49 7.26 7.81 $\bar{X}$ = 7.5200 S^2= 0.0763	7.14 7.12 6.98 $\bar{X}$ = 7.0800 S^2= 0.0076
		Overall Means and Variances for Each Sample			
		n=12 $\bar{X}$ = 7.3517 S^2= 0.0109	n=12 $\bar{X}$ = 7.5392 S^2= 0.0178	n=12 $\bar{X}$ = 7.0075 S^2= 0.1256	n=12 $\bar{X}$ = 7.0133 S^2= 0.0157

Table 7

Analysis EDTA Volume Variance from Experimental Test Series for the Generation II Cement Content Test

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	Computed f	Theoretical $f_{0.01}$
Samples	3	87.2867	29.0956	4.2403	5.92
Subsamples	12	82.3400	6.8617	10.9787*	2.80
Error	32	20.0000	0.6250		
Total	47	189.6267	4.0346		

*Significant at $\alpha = 0.01$

Table 8

Analysis Calcium Analyzer Variance Readings from Experimental Test Series for the Generation III Cement Content Test

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	Computed f	Theoretical $f_{0.01}$
Samples	3	2.4819	0.8273	7.3603*	5.95
Subsamples	12	1.3486	0.1124	6.8957*	2.80
Error	32	0.5223	0.0163		
Total	47	4.3528	0.0926		

*Significant at $\alpha = 0.01$

Results of the analysis of the EDTA volumes indicates that the four samples were the same. However, the analysis indicated significant variability from one subsample to the next. Analyses of the calcium analyzer reading also indicated a difference among samples. Tukeys' test[11] was insensitive to the difference, but Fisher's least significant difference test[12] showed that sample 2 differed from samples 3 and 4, while all other combinations were statistically the same. This result was reasonable in that the sample with the largest overall mean was different from the samples with the two lowest overall means. Scheffe's method[13] for comparing contrasts was used to determine if the difference was caused by the presence of the air-entraining admixture or to the use of different cement suspension tanks. A contrast of nonair-entrained vs air-entrained (samples 1 and 3 vs samples 2 and 4) indicated no difference. A difference was indicated between samples separated in the domestic washing machine and those separated in the fabricated circulating tank (samples 1 and 2 vs samples 3 and 4). Consequently, the sample differences were attributed mainly to the different suspension tanks and probably to different fill marks on the two tanks. Analyses of the calcium analyzer readings also indicated significant variability between subsamples.

It should be noted that the Generation II test could not detect differences in EDTA volumes as large as 3.6 ml. This observation is based on the maximum difference between overall sample means appearing in Table 5 and the analyses results stated above; i.e., the four samples appearing in Table 5 are statistically identical. Following similar reasoning, it appears differences between samples as small as 0.53 units can be detected on the calcium analyzer readout. This is the difference between the overall means of samples 2 and 4 appearing in Table 6. Experimental error variances were 0.6250 and 0.0163 for the EDTA titration volumes and calcium analyzer readings, respectively. The experimental error variance represents the pooled variance for all the subsamples and the expected variance for a given subsample. The smaller the variance, the more likely that differences between samples means can be detected.

Since both analyses indicated significant variability between subsamples, and it was assumed that the cement was dispersed uniformly in the suspension tanks, the remaining source of variability was the sampling procedure.

Generation II sampling was done by the technician attaching a small-diameter hose to an automatic pipet and squeezing the hose. It was important this be done quickly and smoothly. In addition, both the inlet and outlet of the automatic pipe had to be rinsed with 5 percent nitric acid solution after each use, because cement particles remaining from one test could appear in subsequent tests.

Generation III sampling was done using a 30-ml syringe pipet. After prolonged use, the body of the syringe pipet can be enlarged by the abrasive cement particles. Consequently, the syringe must be replaced periodically. It should also be rinsed with 5 percent nitric acid solution after each use.

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[11] S. Wearden and S. Dowdy, Advanced Statistical Methods, Class notes distributed by Department of Statistics (West Virginia University, January 1981).

[12] S. Weardon and S. Dowdy.

[13] S. Weardon and S. Dowdy.

Only one poor subsample was needed for the ANOVA to detect significant variability. Since the subsamples had a random effect on the ANOVA model, statistical procedures could not be used to test for differences among subsamples. However, based on the data, it was conjectured that subsample 3 of sample 2 from the EDTA data in Table 5 and subsample 4 of sample 3 from the calcium analyzer readings in Table 6 were causing the variability. The variability also appeared in the overall variance for these samples; the other subsamples appeared to be the same. However, other subsamples could be the cause of the variability; consequently, it appears that poor subsamples may be obtained from time to time. If this is indeed the case, method accuracy could be improved by using the average of two or more subsamples. This suggestion should be considered in the calibration process. A consequence of adopting this procedure would be a small increase in the time required to complete the test.

The following operational problems were noted during the cement content tests:

1. Cement tended to adhere to the coarse aggregate when the air-entraining admixture was used. The technician had to brush the cement off the aggregate to make sure the cement particles washed into the suspension tank.*

2. The subsample was treated with nitric acid and tap water after it was removed from the suspension tank. The resulting mixture was then stirred with a magnetic stirrer. Since some of the cement particles would cling to the corners or edges of the beaker, the operator had to use a glass stir rod to free the particles.**

3. The washing process was not entirely satisfactory with either the domestic washing machine or the fabricated circulating tank. The latter device splashed more mixture from the tank than the former. The splashing problem seemed to be related to both the fabricated tank's powerful pump and its low-sided sieves. The No. 50 sieve in the fabricated tank could clog, causing the water to back up and overflow through the sieve holes. These holes should be closed to prevent water from escaping. In addition, a baffle plate should be installed to reduce the water velocity. Alternatively, a less powerful pump could be mounted in the tank.***

4. While the pump control level was conveniently located on the domestic washing machine, the lever was not well located on the fabricated tank. This was particularly bothersome when emergencies arose, such as clogged sieves.

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*It was found that the addition of 200 g of "Calgon" water softener to the 10 gal of suspension water aids in the washing process; for Generation III this has been used successfully without chemical interference problems on Roller Compacted Concrete.

**The Generation III method has since been modified to recommend using an Erlenmeyer flask with a magnetic stirring rod whose length is about the same diameter as the flask.

***The Generation III method has since been modified to avoid most of these problems by using a variable transformer to regulate flow.

In addition, the lever on the fabricated tank was either defective or improperly grounded because tank operators received an electrical shock when they touched the wet lever.*

5. The fabricated tank tipped very easily when it was moved. A larger tank base should solve this problem.

6. The fabricated tank should have a standard fill mark. A level indicator should also be built into the tank, and a way to adjust the attitude of the tank so it can be filled accurately. This may be an easily eliminated source of sample variability.**

Generation II Water Content Tests

Eight 2-kg samples were prepared and tested for water content. The test method was similar to that of Generation II (Appendix B). Three water content determinations were made on each sample. Four of the samples used Daravair-R air-entraining admixture so the mixture's effects could be investigated. Aggregate samples were oven dried so the actual-, free-, and total-water contents could be determined.

Before testing, a calibration curve was developed to predict the water content. A simple linear regression equation was developed from the calibration data:

$$y = -70.9653 + 3.6040 \left(X + \frac{\text{Mass sample}}{\text{Mass blank}} (C - B)\right); \; r^2 = 0.9995 \qquad \text{[Eq 6]}$$

where:

y = predicted water content in grams

X = sample KSCN volume in milliliters

C = blank equivalent constant in milliliters

B = blank KSCN volume in milliliters

Mass sample = mass of sample in grams

Mass blank = mass of blank in grams

r^2 = square of correlation coefficient.

All water content predictions were made using Eq 6. A blank was tested for both air-entrained and nonair-entrained concrete. The results were negative for both samples, indicating that chlorides from other sources were not present. Thus, the (C - B) term in the linear regression equation was negligible

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*The Generation III method has since been modified to avoid most of these problems by using a variable transformer to regulate flow.

**The Generation III method's suspension tank is a volumetrically well marked, commercially available "Nalgene" tank; the problems discussed have since been corrected.

and the KSCN volume in milliliters required to reach the sample end point was used directly to predict the water content.

Table 9 lists the KSCN volumes and predicted values from this experiment. The computer pooled variance for each of the samples for the KSCN volumes was 1.0450. The predicted values were converted to percentage recovery so the samples could be compared. Table 10 lists percent recoveries based on free- and total-water; the values in parentheses were based on total-water content. The mean and variance based on free- and total-water contents for each sample are given below the respective data. The overall mean and variance based on free- and total-water contents are listed at the bottom of table.

A nested one-way ANOVA was conducted at the $\alpha = 0.01$ level of significance for percentage recovery based on free-water content. The ANOVA model was:

$$y_{ijk} = \mu + \alpha_i + \beta_{ij} + \varepsilon_{ijk}; \ (\alpha_i \text{ fixed, } \beta_{ij} \text{ random}) \qquad \text{[Eq 7]}$$

where:

y_{ijk} = the effect due to each individual observation

μ = the effect due to the overall mean

α_i = the effect due to air-entraining admixture

β_{ij} = the effect due to sample

ε_{ijk} = the random effect containing all uncontrolled sources of variability due to sampling

Percentage recovery based on free water was choosen as the response variable because previous research results indicated that the results were more representative of free-water than total-water content.[14] Table 11 lists the ANOVA results. The ANOVA indicated that the air-entraining admixtures did not affect the accuracy of the method. The analysis also indicated no significant variability between samples. This was expected because all samples were identical, except for the addition of an air-entraining admixture.

Sampling was a major concern for air-entrained concrete, because at first, it was difficult to obtain a clear sample using the pipet. The test method requires adding 500 ml of 0.5 N NaCl to the sample, mixing for 3 minutes, and allowing the solution to stand for 3 minutes before it can be withdrawn for testing. The sample drawn from the container should be clear and free of solids. (Solids decrease the volume of salt solution, decrease the volume of KSCN required to reach the endpoint, and lead to an erroneously high calculated percentage recovery.) After the sample has been allowed to

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[14] P. A. Howdyshell, IR M-97.

Table 9

KSCN Volumes and Predicted Water Contents from Experimental Test Series for Generation II Water Content Test

		KSCN Volumes (ml)		Predicted Water Contents (grams)*	
		Nonair-Entrained Concrete	Air-Entrained Concrete	Nonair-Entrained Concrete	Air-Entrained Concrete
Samples	1	68.8	70.0	176.9900	181.3148
		69.6	70.6	179.8732	183.4772
		68.4	69.4	175.5482	179.1524
	2	69.6	74.6	179.8732	197.8932
		69.2	72.0	178.4316	188.5228
		73.2	72.2	192.8476	189.2436
	3	70.0	72.6	181.3148	190.6852
		70.0	73.0	181.3148	192.1268
		69.0	73.0	177.7108	192.1268
	4	70.0	71.0	181.3148	184.9188
		70.6	70.2	183.4772	182.0356
		70.0	70.8	181.3148	184.1980
	Blank	99.4	100.0	Actual Water	Actual Water
		100.6	100.2	Total = 190.6	Total = 188.8
Blank Equivalent Constant = 100.4				Free = 176.2	Free = 180.4

*Predicted water content in grams = -70.9653 + 3.6040 x KSCN volume in milliliters.

Table 10

Percentage Recovery from Experimental Test Series for Generation II Water Content Test

		Percent Recovery	
		Nonair-Entrained Concrete Free (Total) Water Basis	Air-Entrained Concrete Free (Total) Water Basis
Samples	1	100.4 (92.9) 102.1 (94.4) 99.6 (92.1) $\bar{X}$ = 100.7000 (93.1333) S^2 = 1.6300 (1.3633)	100.5 (96.0 101.7 (97.2) 99.3 (94.9) $\bar{X}$ = 100.5000 (96.0333) S^2 = 1.4400 (1.3233)
	2	102.1 (94.4) 101.3 (93.6) 109.4 (101.2) $\bar{X}$ = 104.2667 (96.4000) S^2 = 19.9233 (17.4400)	109.7 (104.8 104.5 (99.9) 104.9 (100.2) $\bar{X}$ = 106.3667 (101.6333) S^2 = 8.3733 (7.5433)
	3	102.9 (95.1) 102.9 (95.1) 100.9 (93.2) $\bar{X}$ = 102.2333 (94.4667) S^2 = 1.3333 (1.2033)	105.7 (101.0) 106.5 (101.8) 106.5 (101.8) $\bar{X}$ = 106.2333 (101.5333) S^2 = 0.2133 (0.2133)
	4	102.9 (95.1) 104.1 (96.3) 102.9 (95.1) $\bar{X}$ = 103.3000 (95.5000) S^2 = 0.4800 (0.4800)	102.5 (97.9) 100.9 (96.4) 102.1 (97.6) $\bar{X}$ = 101.8333 (97.3[illegible]) S^2 = 0.6933 (0.6300)
		Overall Means and Variances	
		n=12 $\bar{X}$ = 102.6250 (94.8750) S^2 = 6.1602 (5.3384)	n=12 $\bar{X}$ = 103.7333 (99.1250) S^2 = 9.3806 (8.5784)

Table 11

Analysis of Variance of Percentage Recovery Based on Free-Water Content from Experimental Test Series for Generation II Water Content Test

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	Computed f*	Theoretical $f_{0.01}$
Nonair-entrained vs air-entrained	1	7.3704	7.3704	0.4303	13.75
Samples	6	102.7759	17.1293	4.0202	4.20
Error	16	68.1733	4.2608		
Total	23	178.3196	7.7530		

* None of the computed f values are significant at $\alpha = 0.01$.

stand for 3 minutes, the solids will settle to the bottom. The coarse aggregate will settle first, then the fine aggregate, followed by the cement particles. A clear solution remains on top (see Figure 1, nonair-entrained concrete sample). The pipet tip should be placed just under the surface of the solution to obtain a sample free of solids. The deeper the pipet tip is inserted, the more solids are drawn into the tip. When an air-entraining admixture is used, a thick foam forms on the surface (Figure 1, air-entrained concrete sample). The operator then may find it difficult to locate the clear solution sampling area. The clear sample area can be found by observing the side of the container: different areas indicated in Figure 1 appear as different shades of color in the container.

It was also observed that the longer the sample was allowed to stand, the larger the clear solution sampling area becomes. Thus during testing, it is recommended that the water content samples be prepared first and allowed to settle during the cement content test.

Generation III Water Content Tests

The experimental test series for the Generation III water content test was designed to familiarize the technician with the testing method and to investigate the effects of sample volume and the amount of centrifuging time on chloride meter readings. Various centrifuging times were considered; the sample volume was either 20 or 100 μl. The effects of these two variables were studied with respect to air-entrained concrete because an earlier study had noted a higher than anticipated percentage recovery for air-entrained concrete when Generation III procedures were used.[15]

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[15] P. A. Howdyshell, 1981.

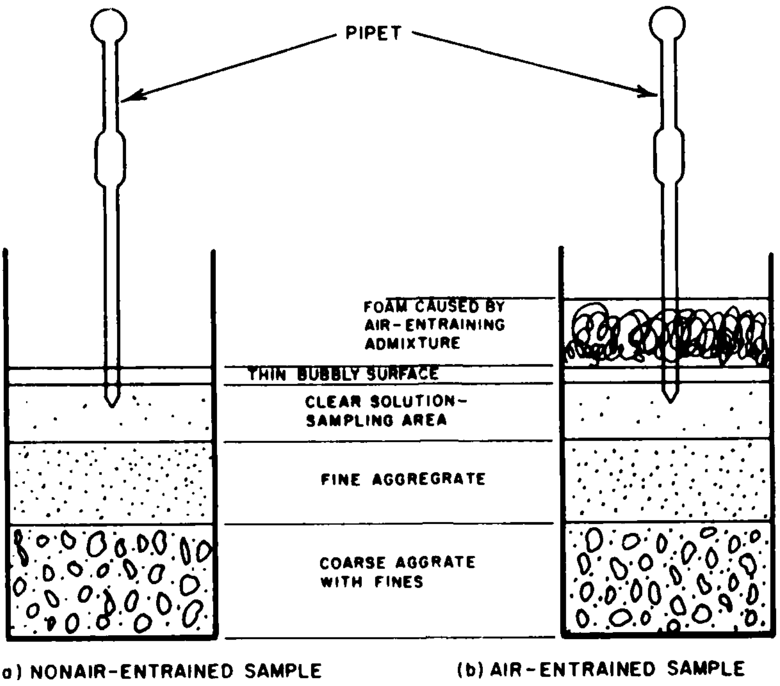

Figure 1. Schematic diagram of the effects of air-entraining admixtures on the Generation II sampling method and proper sampling depth for the Generation II water content test.

At the beginning of the test series, aggregate samples were oven dried to determine their moisture content so corrections could be made for the amount of water present in the mix. Subsequently, a 2-kg sample of concrete was prepared; 250 ml of NaCl were then added to the sample and the solution was mixed for 3 minutes. The intermixed salt solution was poured into individual test tubes which were centrifuged for 60 or 120 seconds. The chloride concentration of the solution was determined using the chloride meter. The pipets were either 20- or 100-μl eppendorf pipets. Data from this experiment are not reported because the results were very erratic. Percentage recoveries based on free-water content were very high, with an overall mean of 122.0 percent and an overall variance of 280.7 for 11 samples.

It was observed that a foam-like surface crust formed in the test tube samples during the centrifuge operation. When the eppendorf pipet tip was inserted through the crust into the test tube, many solid particles were suspended in the liquid phase because of the disturbance caused by the tip piercing the crust. Thus, some solid particles appeared in the sample; this may explain the high percentage recovery values.

The large variance was attributed to the inconsistency of the chloride meter which yielded readings ranging from 42 to 16 for the 20-μl eppendorf pipet and 272 to 207 to 56 to 0 for the 100-μl eppendorf pipet for consecutive readings from the same sample.

To investigate the cause of this inconsistency, various solutions were prepared and tested with the chloride meter using the 20- and 100-μl eppendorf pipets. Table 12 lists these data. Each column in Table 12 represents consecutive readings from the same solution using the indicated eppendorf pipet. A fresh acid buffer solution was used for each set of readings and the electrodes were removed and polished each time, except as noted. The condition cycle reading was also recorded.

Readings obtained from the 20-μl eppendorf pipet were essentially consistent even after the change solution light appeared. When the 100-μl eppendorf pipet was used, readings tended to decrease before the change solution light appeared except for one case, where the readings decreased and the change solution light did not appear. For the 100-μl pipet, the last reading before the change solution light appearance was somewhat lower than previous readings. The legitimacy of those readings is unknown; thus, it should be assumed that the last reading before the change solution light appeared was not a useful value, at least when the 100-μl eppendorf pipet was used.

The chloride meter was specifically designed to determine the amount of chlorides in biological samples. Its instruction manual states that the coulometric titration of chloride is highly reproducible.[16] However, the titration is affected by the presence of sulfide and sulfhydroxyl ions. Erratic behavior of the meter is indicated by nonreproducible values from the sample and black sulfide coating on the electrodes. A black coating is also present during continuous chloride titrations, an effect of AgCl discoloration in the presence of light. The discoloration must be removed periodically with silver electrode polish to ensure reproducible readings.

Because neither the NaCl solution nor the concrete ingredients contained sulfides, the inconsistency of the chloride meter was attributed to continuous chloride titrations. During testing, it was observed that a black coating collected on the electrodes. Consequently, the electrodes were removed and polished each time a fresh acid buffer solution was used. Only the two rear indicator electrodes and the front right generating electrodes were removed for cleaning. The front left generating electrode was removed only when replacement was required.

Based on these observations, it appears that readings tend to decrease as the black coating builds up on the electrodes. To obtain consistent results, it is crucial that the electrodes remain free of the coating. The electrodes should be cleaned with silver electrode polish each time the acid buffer solution is changed. Also, the last reading before the change solution light comes on should be disregarded, particularly when the 100-μl eppendorf pipet is used.

It is recommended that no more than five readings be obtained from the same acid buffer solution when the 100-μl eppendorf pipet is used. Assuming each reading to be 300, a total count of 1500 mEq/L would be obtained. When the 0.5 N NaCl solution (500 mEq/L) is used, no more than three readings should be taken from the same acid buffer solution. The chloride meter instruction manual states that a total count of 200 mEq/L should be obtained

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[16] 920M Chloride Meter Instruction Manual (Corning Glass Works).

Table 12

Chloride Meter Readings for Various Solutions

Solution	NaCl Solution			Non-air-Entrained Concrete		Air-Entrained Concrete		
Sample Size	20 µl	100 µl	100 µl	20 µl	100 µl	20 µl	100 µl	100 µl
Condition Cycle Reading	102	116	Unrecorded*	120	124	128	125	113
	69	500	497	54	293	51	288	288
	104	500	498	55	296	54	287	292
	106	497	496	58	297	52	289	288
	117	491	491	55	292	52	279	292
	115	**	**	57	296	51	285	287
	113	0	479	56	294	53	281	287
	115	0	0	57	289	52	10	280
	114	0	0	58	**	52	32	**
	116		0	56	71	54	1	270
	114			57	4	51	0	92
	115			57	0	53	0	31
	113			56	0	52	+	0
	116			56	0	53		0
	118			56		52		
	119			56		53		
	118			57		53		
	117			58		52		
	**			56		52		
	113			57		54		
	119			55		53		
	119			58		53		
				58		53		
				57		50		
				52		50		
				53		47		
				49		53		
				50		52		
				54		49		
				53		48		
				51		52		
				52		49		
				51		48		
				51		52		
				**		54		
				53		51		
				45		52		
				48		53		
						**		
						53		
						51		
						52		
Total count to appearance of change solution light	1899	1988	1982	1758	2057	1713	1843	2014

*Fresh acid buffer used, but electrodes not polished.

**Indicates appearance of meter change solution light.

+Indicates readings decreased with no indication from meter.

before the change solution light appears. However, when concrete samples were analyzed, readings tended to decrease before the change solution light appeared. The total count corresponding to the appearance of the change solution light for the solutions reported in Table 12 are listed at the bottom of the table.

During testing, it was again observed that air-entrained concrete behaved differently than nonair-entrained concrete. As noted, air-entrained concrete tended to form a surface foam after the sample was centrifuged, making it difficult for an operator to obtain a clear liquid sample. Since nonair-entrained concrete does not foam, it is relatively easy to obtain a clear sample without solids. This problem was very similar to problems encountered during the Generation II water content test. Additional experimentation showed that adequate water content samples were obtained when the operator followed the procedure listed below:

1. Centrifuge the sample.

2. Break up the foam layer and remove the layer with a swab or small spoon.

3. Recentrifuge the sample.

4. Obtain sample for water content analysis.

Based on these observations, a two-factor ANOVA for air-entrained concrete was designed and conducted at the $\alpha = 0.05$ level of significance to determine the effects of sample size and centrifuging method. The ANOVA model was:

$$y_{ijk} = \mu + \alpha_i + \beta_j + \alpha\beta_{ij} + \varepsilon_{ijk} \quad (\alpha_i \text{ fixed}, \beta_j \text{ fixed}) \qquad [\text{Eq } 8]$$

where:

y_{ijk} = the effect due to each individual observation

μ = the effect due to the overall mean

α_i = the effect due to method of centrifuging

β_j = the effect due to sample size

$\alpha\beta_{ij}$ = the effect due to interactions between centrifuging and sample size

ε_{ijk} = the random effect containing all uncontrolled sources of variability due to sampling.

The pilot study results were erratic, so it was not possible to estimate the common variance. It was also noted that the acid buffer solution required for the chloride meter was in short supply. It was decided to take as many samples as possible until the supply of acid buffer solution was exhausted.

The test procedure consisted of fabricating two identical 2-kg samples, adding 250 ml of NaCl, and mixing the samples in an end-over-end mixer for 3 minutes. The intermixed salt solution was randomly poured into individual test tubes which were then centrifuged and tested for chloride concentration. Repeated readings were obtained for the same test tube sample to ensure reproducibility. Test tube samples were centrifuged and tested in groups of four to hasten operations, and to minimize the effect of water evaporation and cement hydration. All test tube samples were assumed to be identical. Four centrifuging methods and two sample sizes were used. The sample volumes were 20 and 100 μl, obtained using eppendorf pipets. The four centrifuging methods were: centrifuging for 60 seconds (60); centrifuging for 60 seconds, using the eppendorf pipet tip to form a hole in the foam on the surface of the sample, and then recentrifuging for 60 seconds (60-hole-60); centrifuging for 180 seconds (180); and, centrifuging for 60 seconds, using a swab to remove as much foam as possible, and recentrifuging for 60 seconds (60-swab-60).

Table 13 lists the chloride meter readings obtained using these procedures. Each cell represents readings obtained from the same test tube sample. Numbers in the sequence column indicate the order in which the data were collected. A "+" or "++" indicates that the solution was changed and/or that the meter behaved erratically.

The same phenomena were observed as reported earlier; i.e., essentially consistent readings were obtained with the 20-μl eppendorf pipet, but when the 100-μl eppendorf pipet was used, readings tended to decrease before the change solution light appeared. In some cases, the change solution light did not appear at all. The light also did not appear one time when the 20-μl eppendorf pipet was used (cell 58). The electrodes were removed and polished each time a fresh acid buffer solution was used.

Water content predictions were made using the average reading obtained in each cell. All readings followed by letters in parentheses, the immediately preceding reading, and obvious outlyers were ignored in computing the average. A blank was tested for each centrifuging method using a 100-μl eppendorf pipet. The results were negative each time. The predicted values were computed from the theoretical relationships:

$$y = 250 \left(\frac{98.6667}{\text{average reading}} - 1 \right) \qquad \text{[Eq 9]}$$

where:

y = predicted water content in grams

average reading = average reading from 20-μl sample.

and

$$y = 250 \left(\frac{502.5000}{\text{average reading}} - 1 \right) \qquad \text{[Eq 10]}$$

where:

average reading = average reading from 100-μl sample.

Table 13

Chloride Meter Readings from Experimental Test Series for Generation III Water Content Tests

Sample Volume and Type	Method of Centrifuging							
	60		60-hole-60		180		60-Swab-60	
	Sequence*	Readings	Sequence*	Readings	Sequence*	Readings	Sequence*	Readings
20-µl Eppendorf Pipet	1	49,52,47	5	48,54,53	9	46,51,51	13	50,53,53
	2	52,52,55	6	48,52,51	10	53,50,52	14	53,51,51
	3	49,51,50	7	50,53,49	11	42,50,49	15	52,51,52
	4	49,52,51	8	50,52,48	12	28+,47,51	16	52,51,51
	57	34,47,58,45,	61	50,53,51	53	49,52,52	49	51,54,53
		45,48,57,41,	62	52,50,52	54	48,49,51	50	52,53,53
		47	63	52,52,53	55	49,52,52	51	54,49,53
	58	52,45,5,0**,	64	52,51,50	56	50,51,50	52	55,52,55
		56,52						
	59	52,51,50						
	60	50,51,51						
100-µl Eppendorf Pipet	17	265,277+,282,	21	275,279,284	25	270,277,259	29	277,278,284
		285,288	22	278,275+,292	26	40**,0,279,	30	278+,285,
	18	282,289,289		282		278,277		284,280
	19	294+,314,295	23	283,281,281	27	271,277,278	31	273,269,248,
		232++,278,	24	272+,283,282,	28	270+,280,280,		59**,281
		281,280		281		286		284,286,
	20	267,263+,275,	45	274,276+,281,	37	261,277,254	32	284,281,281
		282		285		32**,283,288,	33	281+,282,
	41	263,252+,282	46	287,285,286		287		282,289
		282	47	278,284+,280,	38	274,281,278	34a	287,280,274,
	42	280,281,278		280	39	253+,279,	35a	51,19,0**,
	43	280,277+,282,	48	280,278,269		283,282	34b	283,286,288
		282			40	280,283,284	35b	281,280,273
	44	277,277,278					36	231+,281,286,281

*Indicates order in which set of readings was obtained
**Indicates that readings decreased with no warning indication from meter
+Indicates appearance of meter change solution light
++Indicates appearance of meter elec. up light

These values were converted to percentage recovery by dividing them by either 181.5 grams (the actual free-water content) or 195.9 grams (the total-water content). The numbers 98.6667 and 502.5000 represent the average readings obtained from the NaCl solution using the 20- and 100-μl eppendorf pipets, respectively.

Table 14 lists the percentage recoveries based on free-water content. The mean and variance for each data group are also reported. Cochran's test[17] indicated that the variances were unequal, making an ANOVA data analysis invalid. It is obvious which variances are unequal. The cause of the two large variances is unknown; however, the large variances were probably related to the small sample size (20 μl), and the pipet tip breaking through the foam layer and taking up varying amounts of solids each time the procedure was used.

Figure 2 plots the average percentage recovery obtained for each centrifuging method and sample size. The data seem to indicate that the 100-μl eppendorf pipet yields better overall accuracy with less variability than the 20-μl eppendorf pipet for all centrifuging methods. The data also indicate that accuracy is improved when the foam layer is removed from the test tube and the sample recentrifuged (60-hole-60 and 60-swab-60).

Cochran's test indicates that the remaining variances were equal when data for the 60 and 180 centrifuging methods for both sample sizes were excluded from the analysis. Thus, the ANOVA can be used to analyze the remaining data. Eq 8 was used as the ANOVA model; Table 15 lists those results. The ANOVA indicated that the centrifuging method and sample size plus the interaction effect were significant. The significant interaction effect meant that no one method was best for all possible combinations; e.g., the 100-μl eppendorf pipet may be better for the 60-hole-60 centrifuging method, but the 20-μl eppendorf pipet may be better for the 60-swab-60 centrifuging method. Even though the ANOVA indicated significant interactions, they are not evident in Figure 2. Interactions should cause the lines to intersect or at least deviate from parallelism. For the data collected, it appears that the 100-μl eppendorf pipet and the 60-swab-60 or 60-hole-60 centrifuging methods were the best.

These conclusions given above are tentative because test conditions were not identical to those encountered in the field. The test tube samples were random and independent of each other, but the percentage recoveries all depend on one reading from the NaCl solution. In the field, this reading would be obtained for each sample. In addition, obtaining 32 test tube samples from one 2-kg sample may have affected the results.

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[17] R. E. Walpole and R. H. Myers.

Table 14

Percentage Recovery from Experimental Test Series for Generation III Water Content Test for Various Centrifuging Methods and Sample Sizes

		Method of Centrifuging				
		60	60-Hole-60	180	60-Swab-60	
Sample Volume and Type	20-µl-Eppendorf Pipet	137.7	125.3	137.7	123.6	
		118.7	132.3	125.3	125.3	
		134.1	130.5	157.7	125.3	
		130.5	134.1	137.7	127.0	
		152.1	127.0	128.7	120.3	
		118.7	127.0	137.7	120.3	
		128.7	121.9	128.7	123.6	
		130.5	128.7	132.3	113.9	
		n=8 $\bar{X}$=131.3750 S^2=115.2793	n=8 $\bar{X}$=128.3500 S^2=15.4229	n=8 $\bar{X}$=135.7250 S^2=101.9593	n=8 $\bar{X}$=122.4125 S^2=17.4184	n=32 $\bar{X}$=129.4656 S^2=80.6804
	100-µl-Eppendorf Pipet	105.1	110.0	115.3	111.7	
		104.7	103.4	111.2	106.8	
		109.7	107.7	114.9	106.3	
		110.8	107.7	107.7	107.3	
		107.7	106.8	104.3	105.7	
		109.7	104.3	111.7	104.6	
		107.7	109.5	108.3	109.0	
		111.8	113.3	107.4	107.1	
		n=8 $\bar{X}$=108.4000 S^2=6.6086	n=8 $\bar{X}$=107.8375 S^2=10.0855	n=8 $\bar{X}$=110.1000 S^2=14.8257	n=8 $\bar{X}$=107.3125 S^2=4.7698	n=32 $\bar{X}$=108.4125 S^2=9.3018
		n=16 $\bar{X}$=119.8875 S^2=197.6412	n=16 $\bar{X}$=118.0938 S^2=124.1073	n=16 $\bar{X}$=122.9125 S^2=229.6038	n=16 $\bar{X}$=114.8625 S^2=71.1572	n=64 $\bar{X}$=118.9391 S^2=156.8567

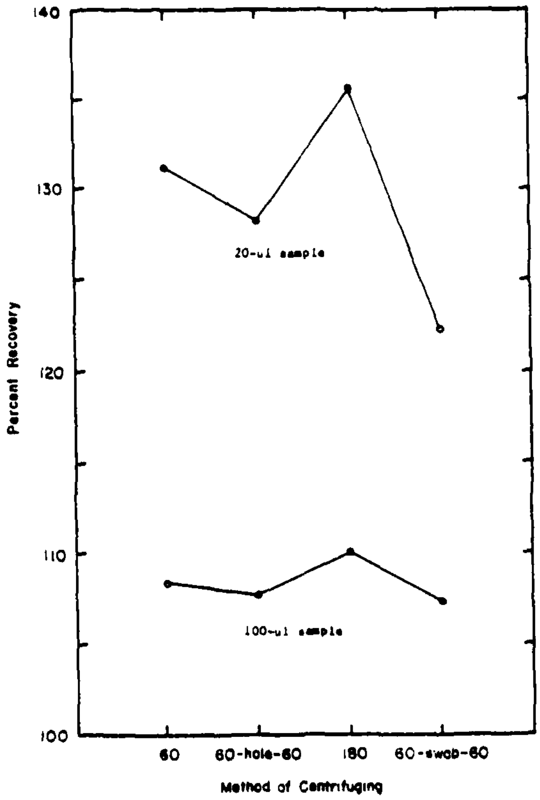

Figure 2. Percentage recovery as a function of sample volume and method of centrifuging in the Generation III water content test.

Table 15

Analysis of Variance of Percentage Recovery Based on Free-Water Content from Experimental Test Series for Generation II Water Content Test for Variance Centrifuging Methods and Sample Volumes

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	Computed f	Theoretical $f_{0.05}$
Method of centrifuging (hole vs swab)	1	83.5278	83.5278	7.0049*	4.20
Sample Size (20 vs 100 μl)	1	2536.5003	2536.5003	212.7187**	4.20
Interaction	1	58.5904	58.5904	4.9136*	4.20
Error	28	333.8762	11.9242		
Total	31	3012.4947	97.1772		

*Significant at $\alpha = 0.05$

**Significant at $\alpha = 0.01$

4 CONCRETE TEST SERIES

In this series, small volumes of concrete were mixed and tested for cement and water content. Both the Generation II and III methods were used.

Materials, Mix Proportions, and Mixing Operations

The concrete test series used Bessemer Type I Portland cement, tap water, Ohio River (siliceous) sand fine aggregate, crushed (calcareous) limestone and Ohio River gravel coarse aggregates, and Daravair-R air-entraining admixture. Thirty-two air-entrained concrete batches were made. Cement for Batches 1 through 24 was supplied by Construction Materials Inc., Morgantown, WV, while cement for Batches 25 through 32 was supplied by the Duntile Company, Morgantown, WV. Mix water was obtained from the West Virginia University Concrete Laboratory. Crushed limestone was used as the coarse aggregate in Batches 1 through 16; Ohio River gravel was used as the coarse aggregate in Batches 17 through 32. Ohio River sand was the fine aggregate in all mixtures. Aggregates required to complete the test series were obtained and stored before testing. (Appendix D lists the characteristics of the aggregates and the air-entraining admixture.) The series used four mixes: w/c ratios were 0.5 or 0.7 while slumps were 2 or 6 in. (51 or 152 mm). Appendix E gives the proportions used for each batch.

The moisture content of the fine aggregate was adjusted to slightly exceed the SSD condition. The aggregate was then stored in a sealed 55-gal (0.2 m^3) drum. The coarse aggregate was soaked in water for about 12 hours. Excess water was allowed to drain for at least 15 minutes before the coarse aggregate was introduced into the mixer. Aggregate samples were oven dried so moisture content determinations could be made before the beginning of each mixing operation.

The inside surfaces of the 3.5-cu ft (0.1-m^3) capacity drum-type mixer were slightly dampened just before the start of each mixing operation. The ingredients were weighed individually and introduced into the mixer in the following sequence: coarse aggregate, sand, cement, and water. The air-entraining admixture was added to the water before the water was added to the mixer. The mixer was allowed to rotate for about 5 minutes. Subsequently, the sample whose volume was about 2 cu ft (0.06 m^3) was discharged into a pan. The concrete was then remixed with a shovel to minimize segregation and to ensure that the ingredients were uniformly distributed before the samples were secured for testing. The concrete was covered with a plasic sheet between sampling operations to minimize water evaporation.

Test Procedures

After the mixing operation was completed, three separate samples were secured for testing using a large scoop. Occasionally, sample mass varied from the desired range of 2 kg ± 200 gram. The samples were tested nonetheless under the premise that altering the sample mass might bias the aggregate/mortar ratio. One of the three samples was used in the Generation II water content test, one in the Generation III water content test, and one in the cement content tests. The latter mass of concrete was processed in the domestic washing machine and two subsamples were obtained. One subsample was used in the Generation II cement test while the other subsample was used in the Generation III cement test. The purpose of this procedure was to minimize the variability caused by sampling.

A 500-ml 0.5 N NaCl solution was added to the Generation II water content sample, which was then mixed in an end-over-end mixer. Following a settling period, a 25-ml sample of the supernatent solution was titrated with potassium thiocyanate. Nitrobenzene was eliminated from the method as a safety precaution. Following titration the sample's water content was predicted using a previously established calibration curve.

In a similar fashion, 250 ml of 0.5 N NaCl solution were added to the Generation III water content sample. The materials were processed as before. Following the mixing operation, the intermixed solution was placed into two separate 15-ml test tubes and centrifuged. The chloride concentration of the supernatent liquid from each test tube was determined using the chloride meter. A 20-μl sample from one test tube and a 100-μl sample from the other were used to determine the chloride concentration. Results were related to sample water content using Eqs 11 through 14, below.

The cement content sample was washed over the No. 4 and No. 50 sieves with recirculating water from the washing machine. After the aggregate was separated from the cement, a representative sample was obtained with a 125-ml linked pipet for the Generation II test. Another representative sample was obtained using a 30-ml syringe pipet for Generation III test.

Two complete sets of cement and water content test results were obtained for each method for each of the 32 batches of concrete. In addition, two 6 in. diameter x 12 in. high (152 mm x 305 mm) cylinders and one 6 in. wide x 6 in. high x 22 in. long (152 mm x 152 mm x 1559 mm) beam were cast from each concrete batch. Slump, unit weight, and mixture air content were determined for each batch. Air content was determined by the pressure method. The cylinders and beams were moist-cured for 28 days and tested to failure in compression and flexure, respectively. The slump, unit weight, air content, and strength tests were all conducted according to American Society for Testing and Materials (ASTM) standard procedures.

Data Analyses

Data from the concrete test series were analyzed to (1) determine the influence of certain test procedures on Generation II and III results, (2) compare Generation II with Generation III, (3) evaluate the effects of coarse aggregate type on Generations II and III, and (4) help establish accuracy statements for both methods. A fundamental assumption was that test accuracies were not affected by cement or water contents. No effort was made to verify this assumption.

Two response variables were used to assess the data: percentage recovery and differences between predicted and actual values. Percentage recovery was used so comparisons could be made with the results of previous studies. It should be noted that percentage recovery values exceeding 100 percent indicate that the predicted value is greater than the actual value; percentage recoveries less than 100 percent indicate the predicted value is less than the actual value. Differences between predicted and actual values were used in the ANOVA to determine if statistically relevant differences existed between certain test procedures and methods and to help develop accuracy statements for Generations II and III. The difference response variable was used to make these decisions because it has a much lower variance than the percentage recovery variable. The smaller the variance, the more reliable the ANOVA when identifying actual differences. It was also believed that accuracy statements based on differences between predicted and actual values had more meaning in a field-use context than did accuracy statements based on percentage recoveries. It should be noted that differences greater than zero between predicted and actual values indicate that the predicted values are greater than the actual values. The converse is true for differences less than zero.

Tables 16 through 18 list mean percentage recoveries and associated standard deviations. Table 16 gives Generation II and III cement test results. Table 17 lists Generation II water test results; Table 18 lists the water test results for Generation III.

Table 16 lists two sets of values for the Generation III cement test results. One set of values used the 20-μl tap water calibration, the other the 100-μl tap water calibration. Both sets were obtained from the same sample, but different calibration curves were used to predict the cement content. Little difference was observed between the two calibration procedures or between Generation II and III cement test results. In all cases, mean percentage recoveries were slightly below 100, indicating that on the average, predicted values were less than actual values. This can be attributed to retention of cement paste (cement plus water) on the mixer's inside walls after the concrete samples were discharged. Most of the aggregate was discharged from the mixer, but some cement paste was retained. Consequently, the theoretical mortar/aggregate mixture ratios were slightly biased by the sampling procedure.

Table 17 lists the Generation II water test results based on free- and total-water contents. Previous studies have indicated that the Generation II water content test was more representative of free-water content than total-water content.[18] These results were also observed during this study; i.e., mean percentage recoveries from the Generation II water content test based on the free-water content were closer to 100 than those based on total-water content.

It should be noted that nitrobenzene was not used in water content tests performed during this study. Because nitrobenzene is toxic and considered a health hazard, it was of interest to determine if nitrobenzene could be eliminated from the method without compromising test results. Nitrobenzene was useful in the Generation II water content test to promote the precipitation of silver chloride, but only very small quantities (about 2 ml) were used per test. Thus, it was believed that eliminating nitrobenzene from the method would not significantly affect test results. Because the water content test results reported here agreed reasonably well with those reported by others

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[18] P. A. Howdyshell, 1977; Howdyshell, 1974.

Table 16

Summary of Cement Content Test Results
Based on Percentage Recovery

Type of Coarse Aggregate		Generation II	Generation III	
			20-µl Tap Water Calibration	100-µl Tap Water Calibration
Limestone	Number of Samples, n	32	32	32
	Mean Percent Recovery, $\bar{X}$	95.78	94.86	94.94
	Standard Deviation, S	7.13	7.56	7.39
River Gravel	Number of Samples, n	32	32	32
	Mean Percent Recovery, $\bar{X}$	98.83	96.30	96.34
	Standard Deviation, S	6.37	7.17	7.10

Table 17

Summary of Generation II Water Content Test
Results Based on Percentage Recovery

Type of Course Aggregate		Results Based on Free-Water Content	Results Based on Total-Water Content
Limestone	Number of Samples, n	32	32
	Mean Percent Recovery, $\bar{X}$	97.17	88.03
	Standard Deviation, S	6.98	5.36
River Gravel	Number of Samples, n	32	32
	Mean Percent Recovery, $\bar{X}$	99.59	83.67
	Standard Deviation, S	3.87	2.28

Table 18

Summary of Generation III Water Content Test Results Based on Percentage Recovery

		Results Based on Free Water				Results Based on Total Water			
		20-µl Test Sample		100-µl Test Sample		20-µl Test Sample		100-µl Test Sample	
		100-µl NaCl Sample	20-µl NaCl Sample	100-µl NaCl Sample	20-µl NaCl Sample	100-µl NaCl Sample	20-µl NaCl Sample	100-µl NaCl Sample	20-µl NaCl Sample
Type of Coarse Aggregate	Method Designation	100/20	20/20	100/100	20/100	100/20	20/20	100/100	20/100
Limestone	Number of Samples	32	32	32	32	32	32	32	32
	Mean Percent Recovery, $\bar{X}$	111.96	111.04	94.67	93.86	101.44	100.60	85.79	85.05
	Standard Deviation, S	8.96	9.76	6.48	7.79	7.38	8.19	5.12	6.51
River Gravel	Number of Samples, n	32	32	32	32	32	32	32	32
	Mean Percent Recovery, $\bar{X}$	118.12	117.31	100.42	99.65	99.20	98.51	84.37	83.72
	Standard Deviation, S	9.28	10.16	5.81	7.43	6.86	7.59	4.56	5.93

(see Table 2), it was surmised that nitrobenzene was not an essential element in the Generation II water content test method. It is recommended that nitrobenzene be eliminated from the test procedure. It should be noted that side-by-side comparison tests, with and without the use of nitrobenzene, were not conducted.

Table 18 lists the Generation III water content test results based on free- and total-water contents. Two test tubes were filled with the intermixed salt solution from the water test sample and centrifuged. The chloride concentration of the intermixed solution was then determined using a 20-μl test sample from one tube and a 100-μl test sample from the other tube. Two water content predictions were then made from each reading. One prediction was made using the 100-μl NaCl sample reading, the other using the 20-μl NaCl sample reading. Thus, for each Generation III water test sample tested, four predicted water contents were calculated. The four predicted values were compared with free- and total-water contents. The results listed in Table 18 for the 20-μl test sample appear to be more representaive of total-water than of free-water content. The results from the 100-μl test sample appear to be more representative of free-water than of total-water content.

The 20-μl test sample results agreed reasonably well with the results of an earlier study of Generation III water tests for air-entrained mixes,[19] however, the earlier studies did not report results based on total-water content and did not evaluate 100-μl samples. That study attributed the high percentage recoveries to the presence of suspended solids not completely settled or removed from the 20-μl test sample. It should be noted that centrifuging was not used in that study.

There is no explanation for the large differences between results for the 20- and 100-μl test samples reported here; centrifuging was used for both methods. The differences were attributed only to sample size. Because results from the 100-μl test sample were more representative of free-water content, and because the general consensus is that the Kelly-Vail water test results represent free-water content, only results from the 100-μl test sample were used to help compare Generation II and III water test methods. All values listed in Tables 16 through 18 are within the range of values reported by other investigators (see Table 2).

Tables 19 through 21 list the mean differences between predicted and actual values. These are the same as those in Tables 16 through 18, except that a different response variable is reported. So all observations noted earlier for Tables 16 through 18 also apply to Tables 19 through 21. The mean differences appearing in Table 19 for the cement test results are all slightly below zero; the Generation II water content test results in Table 20 appear to be more representative of free-water than total-water content; and the Generation III water content test results reported in Table 21 indicate that the 100-μl test sample is more accurate than the 20-μl test sample when free-water content is the standard.

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[19] P. A. Howdyshell, 1981.

Table 19

Summary of Cement Content Test Results Based on Differences Between Predicted and Actual Values

Type of Coarse Aggregate		Generation II	Generation III	
			20-µl Tap Water Calibration	100-µl Tap Water Calibration
Limestone	Number of Samples, n	32	32	32
	Mean Percent Difference, $\bar{X}$	-0.5978	-0.7456	-0.7347
	Standard Deviation, S	0.9739	1.0463	1.0234
River Gravel	Number of Samples, n	32	32	32
	Mean Percent Difference, $\bar{X}$	-0.1250	-0.4406	-0.4353
	Standard Deviation, S	0.9692	1.0272	1.0150

Table 20

Summary of Generation II Water Content Test Results Based on Differences Between Predicted and Actual Values

Type of Coarse Aggregate		Results Based on Free-Water Content	Results Based on Total Water-Content
Limestone	Number of Samples, n	32	32
	Mean Percent Difference, $\bar{X}$	-0.2638	-1.0363
	Standard Deviation, S	0.5481	0.5278
River Gravel	Number of Samples, n	23	32
	Mean Percent Difference, $\bar{X}$	-0.0509	-1.4934
	Standard Deviation, S	0.2958	0.2770

Table 21

Summary of Generation III Water Content Test Results Based on Differences Between Predicted and Actual Values

		Results Based on Free Water Content				Results Based on Total Water Content			
		20-μl Test Sample		100-μl Test Sample		20-μl Test Sample		100-μl Test Sample	
		100-μl NaCl Sample	20-μl NaCl Sample	100-μl NaCl Sample	20-μl NaCl Sample	100-μl NaCl Sample	20-μl NaCl Sample	100-μl NaCl Sample	20-μl NaCl Sample
Type of Coarse Aggregate	Method Designation	100/20	20/20	100/100	20/100	100/20	20/20	100/100	20/100
Limestone	Number of Samples, n	32	32	32	32	32	32	32	32
	Mean Percent Difference, $\bar{X}$	+0.8619	+0.7888	-0.4413	-0.5066	+0.0894	+0.0163	-1.2138	-1.2791
	Standard Deviation, S	0.6292	0.7139	0.5301	0.6548	0.6190	0.7075	0.5164	0.6464
River Gravel	Number of Samples, n	32	32	32	32	32	32	32	32
	Mean Percent Difference, $\bar{X}$	+1.3506	+1.2847	+0.0169	-0.0450	-0.0919	-0.1578	-1.4256	-1.4875
	Standard Deviation, S	0.6433	0.7166	0.4529	0.5942	0.6280	0.6997	0.4488	0.5874

ANOVA techniques in which the difference between predicted and actual values was the response variable were used to:

1. Determine if the Generation III 20-μl and 100-μl tap water calibration procedures for the cement test were statistically different.

2. Compare Generation II cement test results with Generation III cement test results.

3. Determine if the predicted values of the chloride concentration of the intermixed solution in the Generation III water test were statistically different when the 20-μl NaCl sample was used compared to the 100-μl NaCl sample.

4. Compare Generation II water test results with Generation III water test results based on free-water contents.

In all four cases listed above, the effects of coarse aggregate type-limestone vs river gravel were also investigated.

A two-factor ANOVA, conducted at the 0.05 level of significance, was performed for each of the four cases. The ANOVA model was:

$$y_{ijk} = \mu + \alpha_i + \beta_j + \alpha\beta_{ij} + \varepsilon_{ijk} \qquad \text{[Eq 15]}$$

where:

y_{ijk} = the effect of each individual observation

μ = the effect due to the overall mean

α_i = the effect due to each of the four factors described above

β_j = the effect due to coarse aggregate type

$\alpha\beta_{ij}$ = the interaction effect between the method and coarse aggregate type

ε_{ijk} = the random effect containing all uncontrolled sources of variability due to sampling.

with α_j and β_j fixed.

Aggregate type was the second factor. Data for these experimental designs were obtained from Tables 19 through 21 and are repeated in Tables 22, 24, 26, and 28 to show more clearly which factors were compared. The tables also list means and standard deviations for various data combinations. The ANOVA tables (Tables 23, 25, 27, and 29) appear immediately after the respective data table. Cochran's test for the equality of variances indicated that the variances were equal for each cell in each table and for each analysis. Consequently, the assumption of homogenous variances in the ANOVA was satisfied. All four analyses indicated that interaction effects were

Table 22

Generation III Cement Test Results Comparing Calibration Procedures and the Effect of Coarse Aggregate Type

		Generation III Cement Calibration Procedure		
Coarse Aggregate Type		20-µl Tap Water Calibration Data	100-µl Tap Water Calibration Data	
Limestone	Number of Samples, n	32	32	64
	Mean Percent Difference, $\bar{X}$	-0.7456	-0.7347	-0.7402
	Standard Deviation, S	1.0463	1.0234	1.0267
River Gravel	Number of Samples, n	32	32	64
	Mean Percent Difference, $\bar{X}$	-0.4406	-0.4353	-0.4380
	Standard Deviation, S	1.0272	1.0150	1.0130
	Number of Samples, n	64	64	128
	Mean Percent Difference, $\bar{X}$	-0.5931	-0.5850	-0.5891
	Standard Deviation, S	1.0399	1.0223	1.0271

Table 23

Analysis of Variance Comparing Generation III Cement Test Calibration Procedures and the Effect of Coarse Aggregate Type

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	Computed f*	Theoretical $f_{0.05}$
Calibration Procedure (20 µl vs 100 µl)	1	0.0021	0.0021	0.0020	3.92
Aggregate Type (Limestone vs River Gravel)	1	2.9222	2.9222	2.7651	3.92
Interaction	1	0.0002	0.0002	0.0002	3.92
Error	124	131.0472	1.0568		
Total	127	133.9717	1.0549		

* None of the computed f values are significant at $\alpha = 0.05$

Table 24

Cement Test Results Comparing Generation II With Generation III and Effect of Coarse Aggregate Type

Coarse Aggregate Type		Generation II Cement Test Data	Generation III Cement Test Data (100-μl Calibration)	
Limestone	Number of Samples, n	32	32	64
	Mean Percent Difference, $\bar{X}$	-0.5978	-0.7347	-0.6663
	Standard Deviation, S	0.9739	1.0234	0.9934
River Gravel	Number of Samples, n	32	32	64
	Mean Percent Difference, $\bar{X}$	-0.1250	-0.4353	-0.2802
	Standard Deviation, S	0.9692	1.0150	0.9968
	Number of Samples, n	64	64	128
	Mean Percent Difference, $\bar{X}$	-0.3614	-0.5850	-0.4732
	Standard Deviation, S	0.9928	1.0223	1.0099

Table 25

Analysis of Variance Comparing Generation II Cement Test With Generation III Cement Test and Effect of Coarse Aggregate Type

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	Computed f	Theoretical $f_{0.05}$
Cement Test Method (Generation II vs Generation III)	1	1.5998	1.5998	1.6137	3.92
Aggregate Type (Limestone vs River Gravel)	1	4.7702	4.7702	4.8116*	3.92
Interaction	1	0.2407	0.2407	0.2428	3.92
Error	124	122.9291	0.9914		
Total	127	129.5398	1.0200		

*Significant at $\alpha = 0.05$

Table 26

Generation III Water Test Results Comparing Procedures and Effect of Coarse Aggregate Type

Coarse Aggregate Type		Generation III Water Test Procedure		
		100/100 Method	20/100 Method	
Limestone	Number of Samples, n	32	32	64
	Mean Percent Difference, $\bar{X}$	-0.4413	-0.5066	-0.4739
	Standard Deviation, S	0.5301	0.6548	0.5919
River Gravel	Number of Samples, n	32	32	64
	Mean Percent Difference, $\bar{X}$	+0.0169	-0.0450	-0.0141
	Standard Deviation, S	0.4529	0.5942	0.5250
	Number of Samples, n	64	64	128
	Mean Percent Difference, $\bar{X}$	-0.2122	-0.2758	-0.2440
	Standard Deviation, S	0.5409	0.6624	0.6032

Table 27

Analysis of Variance Comparing Generation III Water Test Procedures and Effect of Coarse Aggregate Type

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	Computed f	Theoretical $f_{0.05}$
Water Test Procedure (100/100 vs 20/100)	1	0.1294	0.1294	0.4082	3.92
Aggregate Type (Limestone vs River Gravel)	1	6.7666	6.7666	21.3457*	3.92
Interaction	1	0.0001	0.0001	0.0003	3.92
Error	124	39.3056	0.3170		
Total	127	46.2017	0.3638		

*Significant at $\alpha = 0.05$ and $\alpha = 0.01$

Table 28

Water Test Results Comparing Generation II With Generation III and the Effects of Coarse Aggregate Type

		Water Test Method		
Coarse Aggregate Type		Generation II Water Test Data	Generation III Water Test Data (100/100 Method)	
Limestone	Number of Samples, n	32	32	64
	Mean Percent Difference, $\bar{X}$	-0.2638	-0.4413	-0.3525
	Standard Deviation, S	0.5481	0.5301	0.5423
River Gravel	Number of Samples, n	32	32	64
	Mean Percent Difference, $\bar{X}$	-0.0509	+0.0169	-0.0170
	Standard Deviation, S	0.2958	0.4529	0.3810
	Number of Samples, n	64	64	128
	Mean Percent Difference, $\bar{X}$	-0.1573	-0.2122	-0.1848
	Standard Deviation, S	0.4498	0.5409	0.4962

Table 29

Analysis of Variance Comparing Generation II Water Test With Generation III Water Test and the Effect of Coarse Aggregate Type

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Squares	Computed f	Theoretical $f_{0.05}$
Water Test Method (Generation II vs Generation III)	1	0.0963	0.0963	0.4407	3.92
Aggregate Type (Limestone vs River Gravel)	1	3.6013	3.6013	16.4819*	3.92
Interaction	1	0.4813	0.4813	2.2027	3.92
Error	124	27.0945	0.2185		
Total	127	31.2734	0.2462		

*Significant at $\alpha = 0.05$ and $\alpha = 0.01$

negligible; therefore, interaction effects were excluded from further considerations.

Table 23 lists ANOVA results where the Generation II 20-μl and 100-μl tap water calibrations for the cement test were compared. None of the computed f values were significant, indicating that none of the factors tested contributed to significant test result differences. There was no difference between the Generation III 20-μl and 100-μl tap water calibrations for the cement content test, and aggregate type did not affect the calibrations. The overall mean for the 20-μl tap water calibration, -0.5931, was statistically the same as the overall mean for the 100-μl tap water calibration, -0.5850: an absolute difference of 0.0081. The overall mean for the limestone aggregate, -0.7402, was statistically the same as the overall mean for the river gravel, -0.4380: an absolute difference of 0.3022. This difference was larger than the differences between calibration procedures. In addition, the computed f value for aggregate type in Table 23 was larger than the computed f values for calibration procedures.

Because there were no statistical differences between the two calibration procedures, either could be recommended and compared with the Generation II cement test results. About the same time is required to perform each calibration procedure. Because larger sample volume was generally associated with greater accuracy, results from the 100-μl tap water calibration were compared with results from the Generation II cement content test.

Table 25 lists the ANOVA results where Generation II and III (100-μl tap water calibration) cement test results were compared. There were no differences between the Generation II and III cement content tests in terms of accuracy, as indicated by the given response variable; i.e., the overall mean for the Generation II cement test, -0.3614, was statistically the same as the overall mean for the Generation III cement test, -0.5850: an absolute difference of 0.2236.

Coarse aggregate type affected the accuracy of the cement content test. The overall mean for the limestone coarse aggregate, -0.6663, was statistically different from the overall mean for the river gravel, -0.2802: an absolute difference of 0.3861. It was evident that the means for both Generations II and III are closer to zero for the river gravel coarse aggregate than for the limestone. The analyses indicated that the cement test was more accurate when a river (siliceous) gravel was the coarse aggregate than when a limestone (calcareous) was the coarse aggregate. The difference in accuracy was expected because the limestone aggregate contains calcium; the results of the cement test are directly proportional to the amount of calcium compounds that passed the finest sieve used to separate the sample. The calcium content of a cement from a given source will probably remain relatively constant while the calcium content of a calcareous aggregate from a given source is likely to vary.

Table 27 lists ANOVA results when the NaCl sample sizes used to determine predicted water content were compared. The results indicate no statistical differences between the sampling and calculation methods. The overall means (-0.2122 for the 100/100 method and -0.2768 for the 20/100 method) were statistically the same. Practically, this means that either a 20-μl or 100-μl sample can be used to determine the chloride concentration of the NaCl solution as long as a 100-μl test sample is used to determine the chloride concentration of the intermixed solution. As before, coarse aggregate type had a highly significant effect on the results, indicating that the Generation III water content test was more accurate for one of the aggregates used in the test series. The overall mean for the river gravel, -0.0141, was closer to zero than the overall mean for the limestone, -0.4739; thus, the Generation III water content test was more accurate when siliceous material was the coarse aggregate than when limestone was used as the coarse aggregate.

Table 29 lists the ANOVA results of the comparisons between Generation II and III (100/100 method) water content test methods. There were no differences between the methods in terms of accuracy, as indicated by the given response variable. The overall mean for the Generation II water test results, -0.1573, was statistically the same as the overall mean for the Generation III water test results, -0.2122: an absolute difference of 0.0549. As before, aggregate type had a highly significant effect. The overall mean for the limestone coarse aggregate, -0.3525, was statistically different from the overall mean for the river gravel, -0.0170: an absolute difference of 0.3355. The water test results were affected by the type of coarse aggregate used in the mix. Reviewing the data, it was evident that means for both Generations II and III were closer to zero for the river gravel coarse aggregate than for the limestone. This indicated that the water test was more accurate when a river gravel was used as the coarse aggregate than when a limestone was used. This difference was attributed to physical rather than chemical properties. The river gravel had a much higher absorption capacity than the limestone. It appeared that the water test results were more accurate when a higher absorption capacity coarse aggregate was used than when an aggregate with a low absorption capacity was used.

Accuracy Statements

Accuracy statements were made using the mean difference between predicted values and actual values for Generation II and III cement and water content tests. Because the ANOVA indicated that accuracy was always affected by the coarse aggregate type, the statements were grouped accordingly.

Table 30 presents the 95 percent confidence intervals on the mean difference between predicted and actual values. Generation II and III cement and water test results were calculated using the values in Tables 24 and 28, respectively. The individual means and corresponding variances with 31 degrees of freedom were used to compute the intervals. The values for the combined cement and water tests represented the overall means for the respective aggregate types. The pooled sample variance from Tables 24 and 28 with 124 degrees of freedom was used to compute the interval for the cement and water test results. The pooled sample variance was the same as the error mean square in Tables 25 and 29 for the cement and water tests, respectively. These intervals were included because the ANOVA indicated no difference between the Generation II and III methods within coarse aggregate types.

These accuracy statements apply to a given operator using the specified test procedure for the concrete batches tested. To generalize the accuracy statements, several experiments using other operators and various materials for the concretes tested would have to be conducted.

Table 30

Accuracy Statements Based on 95 Percent Confidence Intervals on Mean Percent Difference Between Predicted and Actual Values

	Limestone Mixes	Ohio River Gravel Mixes
Generation II Cement Test	-0.5978 ± 0.3511	-0.1250 ± 0.3494
Generation III Cement Test (100-μl calibration)	-0.7344 ± 0.3690	-0.4353 ± 0.3660
Combined Cement Test*	-0.6663 ± 0.2464	-0.2802 ± 0.2464
Generation II Water Test	-0.2638 ± 0.1976	-0.0509 ± 0.1067
Generation III Water Test (100/100 method)	-0.4413 ± 0.1911	+0.0169 ± 0.1633
Combined Water Test*	-0.3525 ± 0.1157	-0.0170 ± 0.1157

*Combined Generation II and Generation III data.

Operational Problems

Throughout this study, various problems arose which affected the efficiency of operations. Two major problems occurred with Generation III equipment:

1. The calcium analyzer calibration tended to drift when the analyzer was not operated continuously. Following a period of nonuse, initial readings tended to be excessively high. High readings were observed when the first several batches of concrete were tested. To avoid this problem, the calcium standard solution was tested until readings were within acceptable limits before the unknown cement sample was tested.

2. Chloride meter readings were sometimes erratic. On occasion, readings decreased rapidly for no apparent reason. When this happened, the electrodes were removed and cleaned and a fresh acid buffer solution was used to recondition the chloride meter before testing was resumed. This appeared to correct the problem, but the procedure was time consuming.

5 STRENGTH PREDICTIONS

Concrete strength is affected by many variables. Proper consolidation and curing must occur if the concrete is to attain its maximum potential strength. Aggregate size, shape, surface texture, gradation, and air entrainment also influence strength. However, it is generally accepted that the w/c ratio of a specific type of concrete is the main parameter influencing strength and other indices of quality.[20] Consequently, when methods for determining the water and cement contents of fresh concrete are evaluated, it seems desirable to determine if predicted water and cement content test results can be correlated with concrete strength. CERL has attempted such correlations using a "universal" regression equation for estimating 28-day concrete compressive strength. CERL's studies indicate that in addition to w/c ratio, air content appears to be the only major parameter that influences the compressive strengths of concretes within typical ranges of aggregate type and size.[21] CERL's studies also indicate that the accuracy of strength estimates based on predicted w/c ratios are improved when the relationship between the strength and w/c ratio is known for a given set of materials and mix proportions. This aspect was investigated during this study using regression equations developed for predicting 28-day compressive and flexure strengths. The data used to develop the regression equations were taken from the results of the strength tests described in this report.

All analyses were repeated three times. The actual w/c ratio, the predicted Generation II w/c ratio, and the predicted Generation III w/c ratio were used so differences among predictions based on the three w/c ratios could be assessed qualitatively. Analyses were also performed separately for the limestone coarse aggregate (Batches 1 through 16) and the river gravel mixes (Batches 17 through 32) because the accuracies of the Generation II and III methods were affected by coarse aggregate type. Actual water content was based on free-water content, because free-water content provided better estimates of strength than total-water content.[22] Since this study had demonstrated that Generation II and III predicted water contents were more representative of free-water than total-water contents, average compressive strength and average predicted w/c ratios were used for each batch in the analyses (see Tables 31 and 32).

CERL Procedure for Estimating Compressive Strength

CERL made compressive strength predictions based on a "universal" regression equation. This equation is a function of w/c ratio and air content. If

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[20] Design and Control of Concrete Mixtures, 12th edition (Portland Cement Association, 1979); and G. E. Troxell, H. E. Davis, and J. W. Kelly, Composition and Properties of Concrete, Second Edition (McGraw-Hill, 1968).

[21] P. A. Howdyshell, "Correlating Kelly-Vail Test Results to the Strength Potential of Fresh Concrete," Rapid Testing of Fresh Concrete, Conference Proceedings M-128/ADA009702 (CERL, May 1975).

[22] T. C. Powers, The Physical Structures and Engineering Properties of Concrete, Bulletin 90 (Research and Development Laboratories of the Portland Cement Association, July, 1958).

Table 31

W/C Ratios, Air Contents, and Strength Test Results for Limestone Coarse Aggregate Mixes

Batch No.	Actual W/C Ratio	Generation II Predicted W/C Ratio*	Generation III Predicted W/C Ratio*	Measured Air Content (percent)	Compressive Strength* (psi)**	Flexure Strength (psi)
1	0.50	0.470	0.535	8.5	3740.5	592
2	0.54	0.485	0.510	6.7	5037.5	817
3	0.48	0.500	0.490	4.4	5959.5	875
4	0.48	0.565	0.595	4.4	5190.5	758
5	0.64	0.710	0.680	3.3	3727.5	558
6	0.67	0.660	0.655	3.3	3754.0	600
7	0.72	0.675	0.685	6.0	3014.0	483
8	0.71	0.630	0.625	5.1	2959.5	508
9	0.48	0.475	0.485	6.2	4338.0	658
10	0.51	0.510	0.475	4.6	4818.5	692
11	0.46	0.490	0.460	3.9	5564.5	750
12	0.47	0.475	0.445	4.8	4760.5	733
13	0.67	0.675	0.645	3.7	3541.0	483
14	0.68	0.735	0.665	6.4	3050.5	483
15	0.69	0.740	0.730	6.2	2921.5	492
16	0.71	0.745	0.690	5.4	3060.0	508

*Average of two tests.
**1 psi = 0.0069 MPa

Table 32

W/C Ratios, Air Contents, and Strength Test Results for River Gravel Coarse Aggregate Mixes

Batch No.	Actual W/C Ratio	Generation II Predicted W/C Ratio*	Generation III Predicted W/C Ratio*	Measured Air Content (percent)	Compressive Strength* (psi)**	Flexure Strength (psi)
17	0.48	0.510	0.485	3.8	5443.0	642
18	0.47	0.530	0.470	4.2	5349.5	658
19	0.67	0.680	0.745	8.0	2900.0	458
20	0.69	0.730	0.775	9.0	2363.5	408
21	0.47	0.500	0.490	6.5	4694.5	592
22	0.61	0.485	0.515	6.0	4907.0	650
23	0.68	0.645	0.685	6.6	3166.0	450
24	0.69	0.670	0.715	6.8	3147.5	475
25	0.45	0.440	0.470	2.8	6039.0	675
26	0.48	0.480	0.500	3.0	5694.0	642
27	0.66	0.670	0.675	4.1	3430.5	475
28	0.73	0.765	0.735	5.5	2620.0	425
29	0.47	0.465	0.520	4.8	5007.0	600
30	0.48	0.390	0.410	3.7	6286.5	733
31	0.70	0.735	0.770	5.4	2768.5	450
32	0.69	0.700	0.790	5.1	2880.0	425

*Average of two tests.
**1 psi = 0.0069 MPa

predicted strengths are proportional to actual strengths, the equation's mix calibration factor can improve the accuracy of the predictions. The factor accommodates the effects of other variables that influence strength (admixtures, aggregate type, cement type, etc.). The factor is constant for a given set of materials. The mix calibration factor is the ratio of a data group's actual mean cylinder strength. Typically, mix calibration factors are determined from previous test results or from concrete mix design data. Alternatively, a running average can be used to establish the factor as data become available.

The CERL prediction equation is:[23]

$$f_{28} = A[9551 - 7847\ (w/c) - 733.7(a) + 760.1\ (w/c)(a)] \qquad [\text{Eq } 16]$$

where:

f_{28} = the estimated 28-day compressive strength (psi)

w/c = Generation II or III predicted w/c ratio; actual w/c ratios may also be used.

a = air content in percent

A = mix calibration factor.

The error in estimating the 28-day strengths is computed using standard deviation techniques:[24]

$$\sigma^2 + \frac{\Sigma d^2_i}{n-3} \qquad [\text{Eq } 17]$$

where:

σ^2 = standard deviation of the sample population or standard error

d_i = difference between the actual and estimated strength of the i^{th} case

n = sample population or number of predictions.

The accuracy of the strength predictions was determined with and without the mix calibration factor for the limestone coarse aggregate and river gravel mixes. The actual w/c ratio, the predicted Generation II w/c ratio and the predicted Generation III w/c ratio were used in the analyses.

Table 33 summarizes these results, and shows the mix calibration factors for each, which ranged from 1.183 to 1.214. Standard errors for compressive

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[23] P. A. Howdyshell, 1981; A. J. Nauratil and P. A. Howdyshell, 1979; and H. D. Pritchett, 1978.

[24] P. A. Howdyshell, 1981; A. J. Nauratil and P. A. Howdyshell, 1979; and H. D. Pritchett, 1978.

Table 33

Standard Errors for Compressive Strength Predictions Using CERL Relationship

	Standard Error Without Mix Calibration Factor (psi)*	Value of Mix Calibration Factor	Standard Error With Mix Calibration Factor (psi)
Limestone Coarse Aggregate Mixes			
Actual W/C Ratio	980	1.187	634
Generation II W/C Ratio	1033	1.203	647
Generation III W/C Ratio	1021	1.183	714
River Gravel Coarse Aggregate Mixes			
Actual W/C Ratio	1049	1.195	635
Generation II W/C Ratio	978	1.191	521
Generation III W/C Ratio	1018	1.214	473

*1 psi = 0.0069 MPa

strength predictions computed with the mix calibration factor compared quite favorably to results obtained in previous laboratory evaluations.[25] This factor improved the accuracy of the prediction equation in all cases evaluated. Consequently, the factor was judged a useful parameter for enhancing strength predictions. Also, the magnitudes of standard errors (a measure of accuracy) associated with Generation II and III predicted w/c ratios did not differ greatly from standard errors associated with actual w/c ratios. Thus, both Generation II and III can be used to predict strength potential with errors no greater than those which would occur if strength predictions were based on the actual w/c ratios of the mixes.

Regression Analysis for Predicting Strength

Standard regression techniques were used to develop prediction equations for estimating 28-day compressive and flexural strengths. As before, the analyses were conducted separately for the limestone and river gravel mixes. All analyses were repeated three times using actual w/c ratios, the predicted Generation II w/c ratios, and the predicted Generation III w/c ratios. Average compressive strength and average predicted w/c ratios for Generations II and III were used for each batch. Each regression equation analyzed was based on 16 data points.

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[25] P. A. Howdyshell, 1981; A. J. Nauratil and P. A. Howdyshell, 1979; and H. D. Pritchett, 1978.

Three different regression equations were developed for each case described above. The forms of these equations are:

$$f_{28} = b_0 + b_1 (w/c) + b_2 (a) + b_3(w/c)(a) \qquad [Eq\ 18]$$

$$f_{28} = b_0 + b_1 (w/c) + b_2(a) \qquad [Eq\ 19]$$

$$f_{28} = b_0 + b_1 (w/c) \qquad [Eq\ 20]$$

where:

f_{28} = predicted 28-day compressive or flexure strength (psi)

w/c = actual, Generation II, or Generation III w/c ratio

a = air content in percent

b_0, b_1, b_2, and b_3 are regression coefficients to be determined by the the method of least squares.

Eq 18 is in the same form as the prediction equation developed by CERL. Eq 19 neglects the interaction effect of w/c ratio and air content and Eq 20 correlates strength to w/c ratio only.

The standard deviation, σ, and the correlation coefficient, r, were determined for each regression equation using standard statistical methods. The standard deviation is a measure of the variability of the data points about the regression line. The square of the correlation coefficient, r^2, indicates the variability explained by the model or regression equation. The standard deviation was determined as follows:[26]

$$\sigma^2 = \frac{\Sigma d_i^2}{n-k-1} \qquad [Eq\ 21]$$

where:

σ^2 = standard deviation of the sample population or standard error

d_i = difference between the actual and predicted strength of the i^{th} case

n = sample population

k = number of independent variables in the prediction equation.

The backward elimination process described by Walpole and Myers[27] was used to identify the most acceptable prediction equation. An α-level of significance of 5 percent was used as the decision criterion. In the backward

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[26] R. E. Walpole and R. H. Myers, 1978.

[27] R. E. Walpole and R. H. Myers, 1978.

elimination process, the full model was analyzed and the least significant independent variable was deleted. The new model was then analyzed and the least significant independent variable was deleted again. This process was continued until all independent variables in the prediction equation were significant at the chosen α-level of significance. Although a model might be acceptable, insigificant variables were deleted because such variables could increase the variance of the estimated response.

Tables 34 and 35 summarize these results. Table 34 shows the compressive strength prediction equations; Table 35 contains the flexure strength prediction equations. The results of developing compressive strength prediction equations for the limestone mixes using actual w/c ratios will be described in detail. Other groupings follow the same pattern.

The first model analyzed had the following form (all symbols are as defined in Eqs 18 through 28):

$$f_{28} = 13536.6 - 14366.4\,(w/c) - 838.7\,(a) + 1100.6\,(w/c)(a) \qquad [\text{Eq } 22]$$

The analysis of variance indicated that the model was acceptable at the chosen level of significance with $r^2 = 0.8808$ and a standard error of 392 psi (2.7 MPa). The analysis also indicated that the independent variable (w/c)(a) was the least significant variable.

Next, the independent variable (w/c)(a) was dropped. Thus, the second model analyzed had the following form:

$$f_{28} = 10284.6 - 8657.8\,(w/c) - 212.9\,(a) \qquad [\text{Eq } 23]$$

The analysis of variance indicated that the model was acceptable at the chosen level of significance with $r^2 = 0.8635$ and a standard error of 403 psi (2.8 MPa). The analysis indicated that all independent variables were significant. Consequently, Eq 23 was the most acceptable prediction equation according to citeria inherent in the backward elimination process.

The analysis was repeated to determine if only the w/c ratio could be used to predict strength. This model took the following form:

$$f_{28} = 9117.0 - 8537.8\,(w/c) \qquad [\text{Eq } 24]$$

The analysis of variance indicated that the model was acceptable at the chosen level of significance with $r^2 = 0.7749$ and a standard error of 498 psi (3.4 MPa).

All other groups were analyzed in a similar fashion. In Tables 34 and 35, the most acceptable prediction equation determined using the backward elimination process is marked with an asterisk. All the compressive strength prediction equations determined this way were in the same form as Eq 19, except the river gravel mixes using the Generation III w/c ratio, which were in the same form as Eq 18. All these equations indicated that air content was a significant variable contributing to the prediction of 28-day compressive strength. However, the interaction effect of the w/c ratio and air content

Table 34
Regression Coefficients and Other Statistics for Compressive Strength Prediction
Equations $f_{28} = b_o + b_1(w/c) + b_2\ (a) + b_3(w/c)(a)$

Coarse Aggregate Type	Independent Variable	Intercept	w/c	a	(w/c)(a)		r^2 is square of the correlation coefficient σ is standard deviation or standard error		
	Regression Coefficients	b_o	b_1	b_2	b_3	Acceptable Model	r^2	σ(psi)*	Least Significant Independent Variable
Limestone	Actual	13536.6	-14366.4	- 838.7	1100.6	Yes	0.8508	392	(w/c)(a)
	w/c	10284.6	- 8657.8	- 212.9	--	Yes **	0.8635	403	None
	Ratio	9117.0	- 8547.8	--	--	Yes	0.7749	498	None
	Generation II	14374.3	-14853.0	-1016.8	1253.6	Yes	0.8143	489	(w/c)(a)
	w/c	10384.2	- 7956.4	- 299.2	--	Yes **	0.7812	510	None
	Ratio	8415.8	- 7255.2	--	--	Yes	0.6116	654	None
	Generation III	11490.2	-10748.6	- 454.3	412.1	Yes	0.7570	559	(w/c)(a)
	w/c	10256.5	- 8633.0	- 214.4	--	Yes**	0.7549	539	None
	Ratio	9065.8	- 8496.8	--	--	Yes	0.6651	608	None
River Gravel	Actual	12815.4	-13023.8	- 573.8	640.2	Yes	0.9165	444	(w/c)(a)
	w/c	10975.3	- 9878.5	- 185.6	--	Yes**	0.9121	437	None
	Ratio	11071.8	-11723.2	--	--	Yes	0.8776	497	None
	Generation II	12059.1	-11685.4	- 498.5	501.53	Yes	0.9798	218	(w/c)(a)
	w/c	10598.1	- 9222.9	- 190.0	--	Yes**	0.9757	230	None
	Ratio	10521.3	-10816.8	--	--	Yes	0.9372	356	None
	Generation III	12613.2	-12495.6	- 646.7	772.5	Yes **	0.9823	204	None
	w/c	10209.1	- 8607.7	- 148.9	--	Yes	0.9703	254	None
	Ratio	10150.7	- 9814.8	--	--	Yes	0.9484	323	None

*1 psi = 0.0069 MPa
**Most acceptable equation by the backward elimination process.

Table 35

Regression Coefficients and Other Statistics for Flexure Strength Prediction Equations $f_{28} = b_0 + b_1(w/c) + b_2(a) + b_3(w/c)(a)$

Coarse Aggregate Type	Independent Variable	Intercept	w/c	a	(w/c)(a)		r^2 is square of the correlation coefficient σ is standard deviation of standard error		
	Regression Coefficients	b_o	b_1	b_2	b_3	Acceptable Model	r^2	σ(psi)*	Least Significant Independent Variable
Limestone	Actual w/c Ratio	1791.3	-1894.7	- 99.9	151.9	Yes	0.7548	75	(w/c)(a)
		1342.5	-1106.9	- 13.5	--	Yes	0.7365	75	(a)
		1268.4	-1099.9	--	--	Yes**	0.7165	75	None
	Generation II w/c Ratio	1854.8	-1854.0	-112.7	149.8	Yes	0.7493	74	(w/c)(a)
		1378.0	-1029.9	- 26.9	--	Yes	0.7214	75	(a)
		1200.8	- 966.8	--	--	Yes**	0.6404	82	None
	Generation III W/C Ratio	1348.6	-1095.9	- 15.4	-0.9	Yes	0.6753	84	(w/c)(a)
		1351.4	-1100.7	- 15.9	--	Yes	0.6753	81	(a)
		1263.1	-1090.6	--	--	Yes**	0.6461	81	None
River Gravel	Actual w/c Ratio	1158.1	- 948.5	- 26.9	28.0	Yes	0.8328	50	(w/c)(a)
		1077.7	- 810.9	- 9.9	--	Yes	0.8315	49	(a)
		1082.8	- 909.5	--	--	Yes**	0.8163	49	None
	Generation II w/c Ratio	1102.6	- 863.4	- 18.3	15.1	Yes	0.9383	31	(w/c)(a)
		1058.5	- 789.0	- 9.0	--	Yes	0.9377	30	(a)
		1054.8	- 864.2	--	--	Yes**	0.9245	31	None
	Generation III w/c Ratio	1170.4	- 978.6	- 33.5	44.8	Yes	0.9608	24	(w/c)(a)
		1031.0	- 753.2	- 4.6	--	Yes	0.9545	25	(a)
		1029.2	- 790.7	--	--	Yes**	0.9512	25	None

*1 psi = 0.0069 MPa

**Most acceptable equation by the backward elimination process.

taken together did not contribute significantly to the predicted 28-day compressive strength in five of six prediction equations. It is interesting to note that in every case, an acceptable prediction equation was developed using only the w/c ratio. Thus, reasonable estimates of 28-day compressive strength can be made when only w/c ratio data are available, provided the proper prediction equation is used.

The flexure strength prediction equations were analyzed in the same way. All flexure strength prediction equations determined using the backward elimination process were in the same form as Eq 20. The analyses indicated that flexure strength was independent of air content and that the w/c ratio was the only variable required to estimate 28-day flexure strength.

The standard errors for the compressive strength prediction equations ranged from 204 to 654 psi (1.4 to 4.5 MPa). The standard errors for the flexure strength prediction equations ranged from 27 to 84 psi (0.2 to 0.6 MPa). These values were lower than those associated with the compressive strength prediction equations. It appears that flexure strength can be estimated more accurately than compressive strength. In addition, when standard errors from the actual w/c ratios were compared with standard errors from Generation II and III w/c ratios, it appeared that Generation II and III w/c ratios could be used to predict strength potential with errors no greater than those occurring when strength determinations were based on actual w/c ratios.

Conclusions based on these regression analyses are limited by the amount of data. For example, some statisticians recommend that the number of data points used in multiple regression analyses be 100 or 20 times the number of independent variables, whichever number is larger.[28]

Summary

Results indicate that Generation II and III predicted w/c ratios can be correlated with 28-day concrete strength and used to predict strength potential with an accuracy equal to the accuracy of strengths predicted based on known mix proportions. By using such a system, field personnel could quickly predict concrete strength before the material is placed. Such predictions are potentially useful in preventing the placement of concrete whose strength would be less than a chosen minimum strength. The Generation II and III methods are the only known field techniques that can presently be used to estimate concrete strength with reasonable accuracy before concrete hardens.

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[28] S. Wearden and S. Dowdy.

6 GENERATION III FIELD TESTS AND CHLORIDE METER ASSESSMENT

Field Tests

The Generation III method (the CE/CQM) was tested under field conditions to determine how easy it was to operate, its accuracy, and to identify problems associated with field operation. The field tests were conducted at three West Virginia concrete producers during the fall of 1981. Sites 1 and 2, located in Wheeling, produced highway paving concrete or bridge deck (structural) concrete. Site 3, near Charleston, produced highway paving concrete which contained fly ash as a pozzolanic admixture and partial cement replacement.

The Generation III equipment was set up at each site; materials were obtained from stockpiles at Sites 1 and 3 to help prepare the cement calibration curves. Cement samples were not available at Site 2; consequently, no cement tests were done at that site. Concrete samples for testing were obtained directly from the production facilities at Site 1. Concrete produced at Sites 2 and 3 was sampled at the job location and then transported to the location of the test equipment. This procedure was followed as a matter of convenience with respect to equipment requirements for supplies of water and electricity.

At least four different batches of concrete were sampled and tested at each site over about an 8-hour period. During the field tests, the technician and his assistant had to complete the tests as quickly as possible with due regard for proper equipment operation and cleanup. Maximizing the number of tests performed was not an objective. Four cement content tests were performed at Sites 1 and 3; accompanying these were duplicate or triplicate water content tests except for the first batch at Site 1, where only one water content test was obtained. Only water content tests were performed at Site 2 for the reason noted above.

Laboratory Program

A laboratory program was conducted to determine the effects of selected concrete admixtures on the output of the chloride meter. Six 2-kg samples of concrete, identical except for admixture content, were prepared and tested in the laboratory. Table 36 lists the amounts of ingredients present in each sample. Table 37 describes the admixtures in each of the samples. Manufacturers' descriptions of the admixtures are given in Appendix E.

Table 36

Composition of Samples

Ingredient	Amount
Cement	332.7 g
Water	166.0 g
Fine Aggregate	620.7 g (SSD condition)
Coarse Aggregate	880.6 g (SSD condition)
Admixture	5 ml

Table 37

Mixture Admixtures

Sample Number	Admixture Designation	Admixture Type
1	None	---
2	Daravair-R	Air-entraining agent
3	Sikamix 126 (Sikament)	Water reducer
4	Lubricon R	Set retarder and water reducer
5	Lubricon Rapid Set	Water reducer and set accelerator
6	Sikamix 100 (Plastiment)	Water reducer and set retarder

Sample 1 was the reference mix to which no admixture was added. Samples 2, 3, 4, and 6 were intended to incorporate substances which were reasonably representative of admixtures commonly encountered in field operations. The admixture in Sample 5 was included in the investigation because the admixture contained calcium chloride and it was anticipated that this compound would definitely affect the output of the chloride meter.

The actual testing sequence was as follows:

1. Ingredients were placed into a 0.5 gal (0.02 m^3) container and mixed in an end-over-end mixer.

2. A 250 ml of 0.5 N sodium chloride solution was added to the sample; mixing was then continued for about 3 minutes.

3. Following mixing, three 15-ml samples of the intermixed sodium chloride-cement slurry solution were obtained and centrifuged for 3 to 5 minutes.

4. The test tubes were removed from the centrifuge and observed for the presence of a foam crust near the top of the tube. If present, a small spoon was used to remove the crust and the samples were recentrifuged for 1 minute.

5. The chloride meter was conditioned for testing; the two rear and right front electrodes were cleaned and polished.

6. A test tube was removed from the centrifuge and the chloride concentration of a 100-μl sample was determined using the chloride meter. Meter readings were obtained for additional 100-μl samples until the change solution light appeared on the chloride meter.

7. Steps 5 and 6 were repeated for the remaining two test tubes.

No difficulties were encountered during the testing operations outlined above. Only sample 2 required the foam removal-recentrifuge procedure. The other samples required only one centrifuging operation.

Results

Field Investigations

Table 38 lists the actual quantities of ingredients for the three mixtures tested. The quantities were obtained from producer personnel at the time of testing and subsequently verified from batch quantity records supplied by the West Virginia Department of Highways. Table 39 lists the predicted values of cement and water contents. Table 40 lists the calculated percent recoveries, the mean percent recoveries, and the corresponding standard deviations. Percent recovery is defined in the usual fashion; i.e., 100 times predicted value divided by the actual mixture quantity. Consequently, a value of percent recovery which exceeds 100 percent indicates that the predicted or measured quantity of that ingredient in a particular batch exceeded the desired or target batch weight for the ingredient. Conversely, a value of percent recovery less than 100 percent indicates that the predicted or measured quantity was less than the target batch weight.

Values of mean percent recoveries in Table 40 are all reasonable values in that they are within the spectrum of experience accumulated and reported for results of field tests performed with rapid analysis equipment ranging from Generation I through Generation III. In a similar vein, the calculated standard deviations are also reasonable values. The mean percent recoveries for the cement tests from Sites 1 and 3 and for the water tests from Site 2 were within anticipated limits. Mean percent recoveries for the water tests from Sites 1 and 3 were higher than anticipated. It is noted that at each site, singular percent recoveries exceeding 130 percent were found. It is conceivable that faulty test procedure or undetected equipment malfunctions occurred and that spurious readings were obtained. Eliminating the two values from Table 40 lowers the respective percent recoveries by about 2 percent. Nevertheless, the values are still higher than anticipated. Unfortunately, no explanation is evident for these two apparent anomalies.

No major difficulties were encountered in operating Generation III equipment in the field. A gravity-fed water supply system was used at Site 1; this arrangement was inconvenient when the equipment was cleaned following completion of a test. A pressurized water system should be available when the equipment is used in the field. If such a system is not present, operational efficiency is greatly compromised and the time required to complete a test is

Table 38

Actual Mixture Quantities

Concrete Producer Code/Site No.	Product Tested*	Weight of Ingredients in Pounds (Percent of Total Batch Weight)					Admixtures
		Cement	Water**	Fine Aggregate†	Coarse Aggregate†	Fly Ash	
HWP/1	Paving Concrete	564 (14.76)	243 (6.36)	1125 (29.43)	1890 (49.45)	---	Daravair-R air-entraining admixture
CSC/2	Structural Concrete; bridge deck - Class K	658 (17.53)	255 (6.80)	1100 (29.31)	1740 (46.36)	---	Master Builders air-entraining admixture; Sika set retarder
GER/3	Paving Concrete	470 (12.36)	233 (6.13)	1126 (29.62)	1900 (50.00)	72 (1.89)	Master Builders air-entraining admixture; Master Builders water reducer

* West Virginia Department of Highways designation.

** Free water content

† Ohio River sand and gravel; SSD weights

Table 39

Predicted Values in Percent

Batch Number	Concrete Producer Code/Site No.				
	HWP/1		CSC*/2	GER/3	
	Cement	Water	Water	Cement	Water
1	---	6.68	6.72 7.39	12.64	8.40 6.97
2	13.74	7.06 7.19 8.33	6.68 5.65	13.79	7.20 7.35
3	15.33	7.07 7.79 6.59	7.21 6.58	12.61	7.37 7.56
4	14.16	7.02 6.70	6.80	11.92	7.28 7.03
5	15.18	7.18 7.06	---	---	---

* Water test only was performed. Ingredients for establishing cement calibration curve were not available.

Table 40

Percent Recoveries

	Concrete Producer Code/Site No.				
	HWP/1		CSC*/2	GRK/1	
Batch Number	Cement	Water	Water	Cement	Water
1	---	105.03	98.82 108.68	102.27	137.03 113.70
2	93.09	111.01 113.05 130.97	98.24 83.09	111.57	117.46 119.90
3	103.86	111.16 122.48 103.62	106.03 96.76	102.02	120.23 123.33
4	95.93	110.38 105.35	100.00	96.44	118.76 114.68
5	102.85	112.89 111.01	---	---	---
Number of samples, n	4	11	7	4	8
Mean percent recovery, $\overline{X}$	98.93	112.45	98.80	103.08	120.64
Standard deviation in percent, S	5.25	7.99	8.19	6.27	7.31

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*100 times predicted value in percent divided by actual mixture quantity in percent.

greatly increased. Minor difficulties were experienced during field operations in calibrating the calcium analyzer. The technician resorted to frequent verification using the calcium standard solution to ensure that the analyzer was in proper calibration. Operation of the chloride meter was apparently trouble-free. The technician removed and cleaned the electrodes and a fresh acid buffer solution was used for each sample tested.

Laboratory Program

Results of the laboratory program are summarized in Table 41. The response variable is chloride concentration of the intermixed solution in milliequivalents per liter. The table lists chloride meter readings for each of the three test tubes and for each of the six samples. The number of readings obtained to the appearance of the change solution light (n), the sum of the readings or total count (ΣX), and mean reading ($\overline{X}$) and the variance (S^2) also appear in the table for each test tube. Finally, the table lists the overall mean and variance for each sample. In principle and except for random error, all of the readings should be identical unless the admixture present in the mixture influenced the output of the chloride meter. In addition, the total count to the appearance of the change solution light should be 2000.

It is evident that mean readings from Samples 2, 3, 4, and 6 are lower than the mean readings from Sample 1. Consequently, it appears that the admixtures present in these samples affect the output of the chloride meter. The readings, used as such, would lead to an overestimated concrete sample water content. The cause of the low readings was attributed to a black coating which accumulated on the electrodes of the chloride meter during the continuous titration process.

Table 41

Chloride Meter Readings in Milliequivalents per Liter

Sample No.	1	2	3	4	5	6
Admixture	None	Daravair R	Sikamix 126	Lubricon R	Lubricon Rapid Set	Sikamix 100
Test Tube	312	292	298	295	295	293
No.	311	295	298	293	398	300
	312	292	296	293	395	302
1	308	291	298	294	390	296
	305	282	299	291	390*	292
	300	278	301	291		294
	299*	279*	300*	296*		294*
n	7	7	7	7	5	7
ΣX	2147	2009	2090	2053	1968	2071
$\overline{X}$	306.71	289.00	298.57	293.29	393.60	295.86
S^2	30.57	50.00	2.62	3.57	12.30	14.14
	309	289	293	294	391	298
	309	291	294	293	398	293
	308	292	298	292	398	293
2	302	291	297	304	392	298
	297	291	296	303	388*	293
	297	288	291	292		290
	293*	274*	298*	294*		285*
n	7	7	7	7	5	7
ΣX	2115	2016	2067	2072	1967	2050
$\overline{X}$	302.14	288.00	295.29	296.00	393.40	292.86
S^2	44.14	40.00	7.24	27.00	19.80	20.48
	301	284	295	297	397	288
	305	290	298	293	397	296
	310	288	302	293	397	298
3	307	292	306	296	388	297
	301	287	303	295	393*	296
	293	287	299	292		294
	290*	279*	299*	292*		284*
n	7	7	7	7	5	7
ΣX	2107	2007	2102	2058	1972	2053
$\overline{X}$	301.00	286.71	300.29	294.00	394.40	293.29
S^2	53.00	17.90	13.24	4.00	15.80	27.57
Overall Mean and Variance	21 303.29 44.71	21 287.24 32.69	21 298.05 11.45	21 294.43 11.76	15 393.80 13.89	21 294.00 20.50

*Change solution light appeared

Readings from Sample 5 are much greater than the other readings. As noted previously, it was anticipated that the admixture in Mixture 5 would affect output of the chloride meter because the admixture contained calcium chloride. The high readings would lead to an underestimated water content. The cause of the high readings was attributed to an increase in the chloride concentration of the intermixed solution. It should be noted that the total counts for all test tubes for all samples corresponded to the theoretical total count of 2000 before the meter change solution appeared.

The evidence that common admixtures affect output of the chloride meter is not alarming. Differences between mean readings from Sample 1 and Samples 2, 3, 4, and 6 were relatively small and it is conceivable that the effects of the admixtures in the latter group of samples on the overall accuracy of the method were negligible. This aspect was not considered in the study reported here. Perhaps more importantly, it should be noted that standard operating procedure for the chloride meter includes testing a blank to determine the equivalent chloride concentration of the concrete to be tested. In effect, this procedure allows the operator to compensate for extraneous chloride sources.

Cement Content Tests

1. The accuracies of the Generation II and III cement tests are equivalent for identical test conditions.

2. Aggregate type affects the accuracies of the cement tests. Calcareous aggregate decreases the accuracies of both tests.

3. The poorest average performance was an underestimate of cement content of about 0.73 percent by weight. The best average performance was an underestimate of about 0.13 percent. The 95 percent confidence intervals associated with these average values were ± 0.37 percent and ± 0.35 percent, respectively.

4. On occasion, poor quality subsamples will be obtained from the washing machine or recirculating tank device used in the cement test. Because it is impossible for an operator to visually identify a poor sample, it is recommended that two subsamples be analyzed for each cement test and the results compared. Dissimilar results should be viewed with suspicion. It is also recommended that two or more subsamples be analyzed in the calibration test because all cement test results are related to the calibration curve. Finally, good procedure in the cement tests includes obtaining the subsamples smoothly and rapidly, cleaning the tank and pipets thoroughly after each test, and using identical volumes of water in the washing machine or recirculating tank device each time tests are conducted.

5. There are no differences between the 20-μl and 100-μl tap water calibrations in the Generation III cement test. It is recommended that the 100-μl sample be used to determine the calcium concentration of the tap water in the Generation III calibration procedure.

6. Because the calcium analyzer tends to drift when not in continuous use, it is recommended that the calcium standard solution be tested immediately before samples are tested to verify that the analyzer is in calibration. If the analyzer is not in calibration, the operator should continue testing the calcium standard solution in an attempt to bring the analyzer into calibration. If this procedure is unsuccessful, it will be necessary to recalibrate the analyzer.

Water Content Tests

1. The accuracies of the Generation II and III water content tests are equivalent based on free-water contents for identical test conditions.

2. Aggregate type affects the accuracies of the water tests. Low aggregate absorption decreases the accuracies of both tests.

3. The poorest average performance was an underestimate of free-water content of about 0.44 percent by weight. The best average performance was an overestimate of about 0.02 percent. The 95 percent confidence intervals associated with these average values were ± 0.19 percent and ± 0.16 percent, respectively.

4. The air-entraining admixture used for this study did not affect the accuracy of Generation II water test results. But admixtures can make it difficult to procure solid-free samples. Operators should let samples settle as long as possible and observe the proper sampling depth.

5. In the Generation III water test, air-entraining admixtures will probably produce a thick foam at the top of the test tube after the sample is centrifuged. A centrifuge/breakup and remove/recentrifuge process is recommended when foaming occurs.

6. When Generation III is used and results are based on free-water content, 100-μl samples yield more accurate and less variable test results than 20-μl samples.

7. The results of the Generation II test are more representative of free-water than total-water content.

8. The results of the Generation III test are more representative of total-water content when 20-μl samples are analyzed in the chloride meter, but more representative of free-water content when 100-μl samples are analyzed. Thus, it is recommended that only 100-μl sample volumes be used in the Generation III water content test.

9. The chloride meter output is occasionally erratic. When erratic readings are obtained, it is recommended that a fresh acid buffer solution be used and that the two rear indicator and right-front generating electrodes be removed and polished before they are reused.

Strength Predictions

Both actual and predicted w/c ratios may be used with equal accuracy in relationships developed for estimating 28-day concrete strengths from known w/c ratios. Predicted w/c ratios may be based either on Generation II or III test results.

Generation III Field and Laboratory Tests

1. The Generation III equipment in its present form can be used conveniently and with confidence in the field. The system is relatively easy to transport and to set up under field conditions.

2. Values of cement and water contents predicted using Generation III equipment will probably be within the spectrum of values representing field experience accumulated with all generations of the method.

3. Water content testing of concrete samples containing certain admixtures will require the centrifuge/breakup remove/recentrifuge procedure.

4. The test on admixtures validated the need/requirement for blank samples when admixtures contain chlorides. Other admixtures had negligible effects. (The standard test method requires blank samples to be run.)

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APPENDIX A:

CORNING INSTRUMENTS

The Generation III equipment descriptions in this appendix are taken essentially verbatim from the instruction manuals provided by the instrument manufacturer.

Corning 940 Calcium Analyzer[29]

Replacing manual and colorimetric titration, the calcium analyzer operates on a clinically approved fluorometric quenching procedure based on the fluorescence of calcein in the presence of calcium ions. Fluorometers are instruments which measure the emitted fluorescence of excited molecules. Any light source in the range of 300 to 500 nanometers (nm) may be used to excite molecules in a fluorometer. A primary filter is used to isolate the wavelength of the exciting energy and a secondary filter (at right angles to the exciting beam of light) selects the wavelength to be measured. The intensity of the fluorescent light which strikes the detector is a function of the concentration of fluorescent compound in the cuvette. Fluorometry is a very sensitive sampling tool, generally 100 times more sensitive than spectrophotometry.

Three requirements must be met for the titration to begin: (1) fluorescence must exist in the cuvette, (2) the cuvette must be in its compartment with the door closed, and (3) the titrate button must be pushed. The titration stops when all the calcium has been chelated by the EGTA solution and a predetermined level of fluorescence is attained (this minimal fluorescence being an inherent property of the calcein).

The analytical precision of the calcium analyzer is enhanced by a fluorometer which automatically defines the end point and an electronic calculator which digitally displays the calcium concentration in less than 40 seconds from the sample's insertion. The instrument panel then flashes the ready light and the analyzer is ready to accept the next sample. About 15 samples can be run in one cuvette of reagents after the push button calibration. Easy-to-read indicator lights continuously show the test procedure during the actual sample run. The analyzer will also display an empty cuvette warning when the maximum number of samples has been run to further assure accuracy and prevent overflow into the cuvette chamber. The analyzer is calibrated electronically in less than 3 minutes by the push of a button and will accept sample sizes from 20 μl to 100 μl as long as calibrating and sampling volumes are consistent.

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[29] 940 Calcium Analyzer Instruction Manual (Corning Scientific Instruments, 1973).

Corning 920M Chloride Meter[30]

The operation of the chloride meter is based on the established principle of chloride titration with silver ions generated coulometrically from a silver anode. In coulometric analysis, the unknown sample concentration is proportional to the total current which has flowed during titration. A constant dc voltage applied across a pair of silver electrodes immersed in the diluted sample causes the release of silver ions into the solution containing the sample:

$$Ag \longrightarrow Ag^+ + e^- \qquad \text{[Eq A1]}$$

The silver ions combine with the chloride ions contained in the sample and precipitate as silver chloride:

$$Ag^+ + Cl^- \longrightarrow AgCl \qquad \text{[Eq A2]}$$

When all the chloride has been precipitated, the concentration of silver ions increases, causing the conductivity of the mixture to rise. Sensing electrodes detect this rise in conductance and stop the titration. Since the rate of current flow is constant, the titration of chloride ion is also at a constant rate. The instrument calculates chloride levels directly from elapsed titration time and automatically converts and displays the units of time as milliequivalents of chloride per liter on the digital display.

The coulometric titration of chloride is highly reproducible. However, the titration is affected by the presence of sulfide or sulfhydryl ions. This is indicated by nonreproducible values on the samples and a black sulfide coating on the electrode. The black coating is also present during continuous chloride titrations, an effect of AgCl discoloration in the presence of light. This discoloration must be periodically removed with silver polish to ensure reproducible readings.

The chloride meter is fast and accurate. Simply pipet the sample in the beaker containing 15 to 17 ml of acid buffer, lower the electrodes into the solution, and push the titrate button. The results are displayed in less than 30 seconds and held until the operator begins the next measuring cycle.

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[30] 920M Chloride Meter Instruction Manual.

APPENDIX B:

GENERATION II TEST METHOD DESCRIPTION

Cement Test

Reagents

The reagents required for the Generation II cement content test are:

1. Tap water. A tap water supply should be readily available for filling the washing machine, washing cement through the sieves, and diluting samples. The tap water used to prepare the calibration curve should come from the same source as that used to make the concrete.

2. Distilled water is needed to make the testing solutions.

3. Nitric acid solution (5 percent). Add one volume (5 ml) of concentrated nitric acid (HNO_3, specific gravity 1.42) to 19 volumes (95 ml) of distilled water. Always add acid to the water.

4. Ammonia ammonium chloride buffer solution (pH = 10). Add 142 ml of ammonium hydroxide (NH_4OH, assay as NH_3 w/w 28 to 30 percent, specific gravity 0.88 to 0.90) to 17.5 grams of ammonium chloride (NH_4Cl). Add distilled water until 250 ml of solution are obtained. This solution should always be covered when not in use since the ammonia in the buffer solution evaporates quickly.

5. Eriochrome black T indicator solution. Dissolve 0.5 gram of eriochrome black T (color index no. 14645) in 25 ml of triethanolamine. This solution has limited stability. The age of the solution affects the accuracy of determining the end point in the titration process. The eriochrome black T indicator solution should not be allowed to age more than 2 months. When this solution is prepared, the preparation and expiration dates should be written on the container label. At the expiration date, a new solution should be made and a new calibration curve constructed before further tests are conducted.

6. Sodium ethylenediaminetetraacetate (0.01 M). Dissolve 3.72 grams of disodium ethylenediaminetetraacetate dihydrate (EDTA) in about 100 ml of distilled water. Add distilled water until 1L of solution is obtained. EDTA solutions should be stored in polyethylene containers. When stored in glass bottled, EDTA solutions gradually leach metal ions out of the glass, which changes their effective concentration. This does not happen if polyethylene containers are used.

Cement Test Procedure

The cement content test steps are:

1. Prepare necessary reagents.

    a. Nitric acid solution (5 percent).

    b. Tap water.

c. Ammonia ammonium chloride buffer solution.

d. Eriochrome black T indicator solution.

e. EDTA solution.

2. Prepare equipment and reagents for use.

a. Fill washing machine with 10 gal (37.6 L) of tap water to the fill mark. The tap water used to fill the washing machine should come from the same source as that used to prepare the calibration curve and make the concrete.

b. Place nested sieves (No. 4 and No. 50) on the washing machine.

c. Charge the automatic pipets with their appropriate reagents, i.e., 100 ml of 5 percent nitric acid and 300 ml of tap water.

d. Fill the 100-ml buret with 0.01 M EDTA solution.

3. Obtain a 2-kg ± 200 gram sample of fresh concrete in a 0.5 gal (1.8 L) polyethylene wide-mouth jar and record the mass to the nearest gram. The sample of concrete from which the cement content test specimen is made must be representative of the entire batch. The sample should be well mixed to ensure homogeneity.

4. Transfer the test specimen to the sieves nested over the washing machine and turn on the washing machine recirculating pump and agitator. Wash the residue from the sample into the washing machine using the jet of water from the recirculating pump hose. Keep the jet of water moving slowly over the surface of the sieve to avoid loss of the suspension by splashing.

a. Be sure to put all material from the sample container onto the washing machine's nested sieves.

b. Wash the plus No. 4 material carefully, using the jet of water from the recirculating pump hose. After all the minus No. 4 material has been washed through the sieve (this usually takes 1 to 1.5 minutes), remove the No. 4 sieve and its contents.

c. Wash the plus No. 50 material carefully, using the jet of water from the recirculating pump hose. After all the minus No. 50 material has been washed through the sieve (this usually takes 1 to 1.5 minutes) remove the No. 50 sieve and its contents.

5. After the sample has been washed through the sieves, obtain a representative sample (125 ml) of the suspension in the washing machine by using the small hose. Clamp the large hose when using the small hose to take a sample.

a. Squeeze the end of the large bore recirculating hose to force the suspension to flow through the T piece and the 1/4-in. inner diameter tubing.

b. Rapidly release the large bore recirculating hose so the suspension will flow through it; connect the end of the 1/4-in. inner diameter tubing to the 125-ml linked pipet.

c. Squeeze the large bore recirculating hose again to direct the suspension into the pipet. When the pipet is filled to the overflow device, switch off the lower pipet tap and release the large bore recirculating hose.

6. Drain the 125-ml sample from the automatic pipet into a mixer cup or beaker that has a capacity of at least 800 ml.

7. Wash out the 125-ml linked pipet using 100 ml of the 5-percent nitric acid solution from the automatic pipet positioned above the 125-ml pipet. The acid solution will drain through the 125-ml linked pipet and into the mixer cup.

8. Add 300 ml of tap water from the third automatic pipet to the mixer cup.

9. Fix the mixing cup to the stirrer for 3 minutes to insure a homogenous solution. A mixing cup and stirrer can be used instead of a beaker and magnetic stirrer. If a magnetic stirrer is used, place a teflon magnetic stir rod in the beaker and place the beaker on a magnetic stirrer for three minutes.

10. After stirring is completed, pipet off 25 ml of the resulting solution and place in a 500-ml conical beaker.

11. Using an automatic pipet, add 10 ml of ammonia ammonium chloride buffer solution and 4 to 6 drops of eriochrome black T indicator solution from a dropper. The same number of drops should be used in both calibration and test samples. To obtain a clear and distinct end point, the buffer solution must be added before the indicator solution. Shake well by hand for a few second.

12. The relative calcium concentration of the solution in the 500-ml beaker is determined by an EDTA end point titration using a 100-ml buret. Titrate the solution (wine color) with a 0.01 M EDTA solution until the end point (blue) is reached. The end point is reached when the solution turns from a wine color to a pronounced blue. Swirl the contents of the beaker during titration. Some operators prefer to perform the titration with the beaker and solution on a magnetic stirrer. This ensures that the solution is well mixed. It is recommended that operators not wear tinted (sun) glasses during the calcium titration process. Tinted glasses can alter the perception of when the wine colored solution turns to the blue end point. This test cannot be performed by people who are color blind.

13. Record the volume of EDTA solution (in milliliters) required to reach the end point for the unknown sample. Repeat Steps 10 through 13, as necessary, to assure reproducibility.

14. The cement content of the sample (in grams) can now be estimated by referring to a previously established calibration curve for the cement type and materials being used.

15. Empty and clean the washing machine for next test.

Calibration Requirements

Before testing for cement content, a calibration curve must be obtained for the calcium in the water and the concrete to be tested. This is done by performing a standard cement test on plain tap water and a 2-kg calibration sample of concrete prepared using the materials and mix proportions of the concrete to be tested. An EDTA titration is performed on the tap water and the calibration sample. The volume of EDTA required to reach the end point for the tap water represents 0 g of cement; the volume of EDTA required to reach the end point for the concrete calibration sample represents the mass of cement in the calibration sample. All unknown cement contents are linearly proportional. It is recommended that new calibration data be established whenever: (1) the cement source or type used to produce the concrete is changed or on a weekly basis if the cement source or type does not change, (2) the aggregate source is changed, (3) the design mix is changed, or (4) the strength of the reagents is changed or fresh reagents are made.

The tap water calibration is performed as follows:

1. Prepare necessary reagents as described in Step 1 of the cement test procedure.

2. Prepare equipment and reagents for use.

   a. Charge the automatic pipets with their appropriate reagents, i.e., 100 ml of 5-percent nitric acid and 300 ml of tap water.

   b. Fill the 100-ml buret with 0.01 M EDTA solution.

3. Place 125 ml of tap water in a mixing cup or beaker of at least an 800-ml capacity.

4. Add 100 ml of 5-percent nitric acid solution from an automatic pipet.

5. Follow Steps 8 through 13 of the cement test procedure. The volume of EDTA solution required to reach the end point represents 0 g of cement and gives one point on the calibration curve.

The concrete calibration sample is tested as follows:

1. Prepare necessary reagents as described in Step 1 of the cement test procedure. Also hand mix a 2-kg concrete calibration sample using the materials and mix proportions of the concrete to be tested. The materials used to prepare the calibration sample must be the same as those in the concrete being tested. All materials must be obtained from the stockpiles used to produce the concrete.

2. Prepare equipment and reagents for use as described in Step 2 of the cement test procedure.

3. Transfer the calibration sample to the sieves nested over the washing machine and follow Steps 4 through 13 of the cement test procedure. Repeat Steps 5 through 13 of the cement test procedure, as necessary, to verify that a representative subsample was obtained. The volume of EDTA solution required to reach the end point represents the mass of cement in the calibration sample and gives another point on the calibration curve.

4. To construct the linear calibration curve of cement content in grams vs the volume of EDTA required, plot (a) 0 g of cement and the volume of EDTA required for the tap water calibration, (b) the mass of cement in the 2-kg concrete calibration sample and the volume of EDTA required for the calibration sample. Connect these two points to complete the calibration curve. All unknown cement contents are linearly proportional.

5. Since the calibration curve is a straight line determined by two points, a linear equation can be developed as follows:

$$\text{Cement content (gram), } y = (X-T)\left(\frac{W}{S-T}\right) \qquad \text{[Eq B1]}$$

where:

y = cement content of sample in grams

X = EDTA volume in milliliters required to reach the end point for the sample

W = mass of cement in the 2-kg concrete calibration sample (in grams)

T = EDTA volume in milliliters required to reach the end point for the tap water calibration

S = EDTA volume in milliliters required to reach the end point for the 2-kg concrete calibration sample.

The cement content can be stated as a percentage by dividing the predicted value by the mass of the sample tested and multiplying by 100.

Water Test

Reagents

Eight reagents are required for the water content test:

1. Distilled water is needed to make testing solutions and to dilute the blank used to determine chlorides in the concrete.

2. Tap water is needed to make the sodium chloride solution and to prepare the calibration curve. The tap water used must come from the same source as that used to make the concrete.

3. Sodium chloride solution (0.05 N). Dissolve 292.2 g of dry sodium chloride (NaCl) in tap water. Add tap water until 10 L of solution are obtained. Since dry NaCl crystals dissolve slowly, it is recommended that mechanical agitation be used to assure that the NaCl crystals are completely dissolved.

4. Silver nitrate solution (0.05 N). Dissolve 255.0 g of dry silver nitrate ($AgNO_3$) in distilled water. Add distilled water until 3 L of solution are obtained.

5. Potassium thiocyanate solution (0.05 N). Dissolve 24.3 g of dry potassium thiocyanate (KSCN) in distilled water. Add distilled water until 5 L of solution are obtained.

6. Nitric acid solutin (50 percent). Mix equal volumes of concentrated nitric acid (HNO_3, specific gracity 1.42) and distilled water. Carefully add one volume of concentrated nitric acid to one volume of distilled water. Always add acid to water.

7. Ferric alum indicator solution. Dissolve 50 g of ferric ammonium sulphate ($Fe(NH_4)_2(SO_4)_2 \cdot 6\ H_2\ O$) in 100 ml of distilled water and add five drops of 50 percent nitric acid solution.

8. Nitrobenzene ($C_6H_5NO_2$, specific gravity 1.20). Use full-strength American Chemical Society (ACS) grade. Nitrobenzene is extremely toxic and is rapidly absorbed through the skin. Contact with skin or clothing and inhalation of fumes and vapors should be avoided. Due precaution should be observed when using this reagent.

Water Test Procedure

The water content test is carried out as follows:

1. Prepare necessary reagents:

   a. Distilled water

   b. Sodium chloride solution (0.5 N)

   c. Silver nitrate solution (0.5 N)

   d. Potassium thiocyanate solution (0.05 N)

   e. Nitric acid solution (50 percent)

   f. Ferric alum indicator solution

   g. Nitrobenzene.

2. Obtain two 2-kg ± 200 g samples of fresh concrete. Place each in separate 0.5-gal polyethylene wide-mouth jars and record the mass to the nearest gram. The sample of concrete from which the water content test specimens are made must be representative of the entire batch. The sample should be well mixed to ensure homogeneity.

3. Using a volumetric flask, add 500 ml of 0.5 N sodium chloride solution to one jar. This is the sample required for estimating the water content of the concrete. Add 500 ml of distilled water to the other jar. This is the blank required for estimating chlorides in the concrete. If the concrete being tested does not contain chlorides, use of the blank may be discontinued after the inital determination.

4. Secure watertight lids on both containers.

5. Turn the two jars end-over-end in a 40 to 60 rpm mixer for at least 3 minutes. Under no conditions should the jars be turned so rapidly that the centrifugal forces exceed gravitational forces, thereby inhibiting the complete intermixing of the salt solution (sample) and distilled water (blank) with the concrete samples.

6. Remove the jars from the mixer, loosen the lids, and allow the contents of each jar to settle for at least 3 minutes.

7. Using a volumetric pipet, withdraw 25 ml of the clear supernatent solution from the sample and place in a 500-ml conical beaker. Using a volumetric pipet, withdraw 25 ml of the clear supernatent solution from the blank and place in a 500-ml conical beaker.

8. Using an automatic pipet, add 25 ml of 0.5 N silver nitrate solution to the sample solution. Using an automatic pipet, add 10 ml of 0.5 N silver nitrate solution to the blank solution.

9. Using an automatic pipet, add 10 ml of 50 percent nitric acid solution to both the sample and the blank.

10. Using an automatic pipet, add 5 ml of ferric alum indicator solution to both the sample and the blank.

11. Using an automatic pipet, add 2 ml of nitrobenzene to both the sample and the blank.

12. Shake both the sample and the blank by hand for a few seconds to coat the silver chloride precipitate.

13. The relative chloride strength of the sample and blank solutions in the beakers are determined by titration using the 0.05 N KSCN solution in a 100-ml buret. The chloride strength of the sample solution can be determined by initially adding (with an automatic pipet) 25 ml of 0.05 N KSCN solution. The titration is then completed with a 100-ml buret. The chloride strength of the blank solution is determined using a 100-ml buret only. Swirl the contents of the sample and blank beakers during titration. Some operators prefer to perform the titration with the beaker and solution on a magnetic stirrer. This ensures that the solution is well mixed. Stop titration when the first permanent reddish brown (rust) color appears: the end point has been reached. The white to reddish brown end point can be rather difficult to identify and requires careful observation. The end point has been reached when the solution reaches its first tint of a permanent reddish brown color. After the first permanent reddish brown color has been attained, continued

agitation of the solution can cause the reddish brown color to disappear momentarily.

14. Record the volume in milliliters of 0.05 N KSCN solution required to reach the end point for both the sample and the blank. Repeat Steps 7 through 14, as necessary, to assure reproducibility.

15. The water content of the sample can now be estimated by referring to a previously established calibration curve. The blank equivalent constant and blank test results must be considered if the concrete contains chlorides from sources other than the mix water. (The procedure for preparing the calibration curve and determining the blank equivalent constant is described below.) The blank test results are subtracted from the blank equivalent constant and added to the sample test results to obtain the total KSCN volume as follows:

$$\text{Total KSCN volume (ml)} = X + \frac{\text{Mass sample}}{\text{Mass blank}}(C-B) \qquad \text{[Eq B2]}$$

where:

X = sample KSCN volume in milliliters

C = blank equivalent constant in milliliters

B = blank KSCN volume in milliliters

Mass sample = mass of sample in grams

Mass blank = mass of blank in grams

If the concrete being tested does not contain chlorides ($C-B = 0 \pm 2$ ml), use of the blank may be discontinued after the initial determination.

16. The water content of the unknown sample is determined by relating the total KSCN volume to the water content vs potassium thiocyanate curve.

Calibration Requirements

The water calibration curve is established by performing a standard water content test on 100, 150, and 200 grams (100, 150, and 200 ml) samples of water. The corresponding volume in milliliters of 0.05 N KSCN solution required to reach the end point for each of the different quantities of water used represents a concrete specimen containing 100, 150, and 200 grams (100, 150, and 200 ml) of water, respectively. The calibration data are plotted and a smooth curve is drawn through the data points. The calibration curve can be used directly in the field for determining unknown water contents. For more accurate readings from the calibration curve, a linear regression equation can be developed from the three sets of data points using standard statistical methods.

If the concrete to be tested contains chlorides from other sources, the volume of 0.5 N KSCN solution required to reach the end point for the sample will be reduced; the indicated water content of the concrete will be less than the actual water content. This potential discrepancy is accounted for by testing a blank to determine the equivalent volume of 0.05 N KSCN solution that must be added to the sample test results before the water content of an unknown sample is determined from the calibration curve. A blank equivalent constant is used for this purpose. The calibration procedures are required each time fresh reagents are made or on a weekly basis.

The blank equivalent constant is determined as follows:

1. Using an automatic pipet, place 10 ml of 0.5 N silver nitrate solution into a conical beaker of at least a 500-ml capacity.

2. Using an automatic pipet, add the following to the beaker containing the 10 ml of 0.5 N silver nitrate solution:

   a. Ten milliliters of 50 percent nitric acid solution.

   b. Five milliliters of ferric alum indicator solution.

   c. Two milliliters of nitrobenzene.

3. Shake well by hand for a few seconds.

4. Titrate using the 0.5 N KSCN solution from a 100-ml buret. Swirl the contents of the beaker during titration. Stop titration when the first permanent reddish brown color appears; this denotes the end point.

5. Record the volume in milliliters of 0.05 N KSCN solution required to reach the end point. This volume is the blank equivalent constant. If the reagents were mixed correctly, the blank equivalent constant should have a value of 100 ± 2 ml. Repeat Steps 1 through 5, as necessary, to assure reproducibility.

The procedure for establishing the calibration curve for determining the water content of fresh concrete is as follows:

1. Obtain 100 grams (100 ml) of water and place in a 0.5 gal polyethylene wide-mouth jar. The water used for calibration must come from the same source as that used to make the concrete to be tested.

2. Using a volumetric flask, add 500 ml of 0.5 N sodium chloride solution.

3. Secure a watertight lid on the container and mix in a 40 to 60 rpm mixer for at least 3 minutes.

4. Remove the jar from the mixer and loosen the lid.

5. Using a volumetric pipet, withdraw 25 ml of the intermixed solution and place in a 500-ml conical beaker.

6. Using an automatic pipet, add 25 ml of 0.5 N silver nitrate solution to the beaker.

7. Using the automatic pipet, add the following to the beaker:

a. Ten milliliters of 50 percent nitric acid solution.

b. Five milliliters of ferric alum indicator solution.

c. Two milliliters of nitrobenzene.

8. Shake well by hand for a few seconds.

9. Titrate (100-ml buret) using the 0.05 N KSCN solution. Swirl the contents of the beaker during titration. Stop the titration when the first permanent reddish brown color appears.

10. Record the volume in milliliters of 0.05 N KSCN solution required to reach the end point. This is the volume of 0.05 N KSCN solution required for a chloride-free concrete specimen containing 100 grams (100 ml) of water. Repeat Steps 5 through 10, as necessary, to assure reproducibility.

11. Repeat Steps 1 through 10 using 150 grams (150 ml) and 200 grams (200 ml) of water. The data should be recorded as follows:

Water Calibration Sample (gram), W	KSCN Volume (ml), V
$W_1 = 100$	V_1
$W_2 = 150$	V_2
$W_3 = 200$	V_3

where W is mass of water in the water calibration sample and V is the corresponding volume of 0.05 N KSCN required to reach the end point.

12. Plot the results of water content in grams vs the volume of 0.05 N KSCN required in milliliters. Draw a smooth curve through the calibration data.

13. A linear regression equation can be developed from the three sets of data points as follows:

$$\text{Water content (gram), } y = i + m\left(X + \frac{\text{Mass sample}}{\text{Mass blank}}(C - B)\right) \qquad \text{[Eq B3]}$$

where:

y = water content of sample in grams

X = sample KSCN volume in milliliters

C = blank equivalent constant in milliliters

B = blank KSCN volume in milliliters

Mass sample = mass of sample in grams

Mass blank = mass of blank in grams

i and m = coefficients determined from regression analysis

$$m = \frac{3\Sigma WV - 450\ \Sigma W}{3\Sigma V^2 - (\Sigma V)^2}$$

$$i = 150 - \frac{\Sigma V}{3}(m)$$

The square of the correlation coefficient can be determined as follows:

$$r^2 = \frac{(3\Sigma WV - 450\ \Sigma V)^2}{(15000)(3\Sigma V^2 - (\Sigma V)^2)} \qquad \text{(Eq B4)}$$

The water content can be stated as a percentage by dividing the predicted value by the mass of the sample tested and multiplying the result by 100.

APPENDIX C:

GENERATION III TEST METHOD DESCRIPTION

Cement Test

Reagents

The reagents required for the cement content test are:

1. Tap water. A tap water supply should be readily available for filling the tank, washing cement through the sieves, and diluting samples. The tap water used to prepare the calibration curve should come from the same source as that used to make the concrete.

2. Distilled water is needed to make a 5-percent nitric acid solution.

3. Nitric acid solution (5 percent). Add one volume (5 ml) of concentrated nitric acid (HNO_3, specific gravity 1.42) to 19 volumes (95 ml) of distilled water. Always add acid to water.

4. EGTA solution. The EGTA solution, supplied in a plastic bottle, is to be installed in the open side compartment of the analyzer.

5. Potassium hydroxide solution (1.0 N KOH).

6. Calcium standard solution (10 mg %, 5 mEq/L).

7. Calcein indicator solution. A calcein indicator (dry powder) is supplied in an opaque bottle and is to be reconstituted with 10 ml of the calcium standard solution. Measure the dilutent carefully into the bottle, mix thoroughly, and allow to stand at least 10 minutes before using. Care should be taken not be contaminate the calcium standard solution when reconstituting the calcein indicator. The reconstituted calcein indicator solution is stable for 4 weeks at 22°C, after which it must be discarded. The date the indicator is reconstituted and its expiration date must be clearly written on the bottle's label. Each bottle contains enough indicator for about 1500 tests.

Reagents 4 through 7 are preprepared reagents available from the calcium analyzer manufacturer.

Cement Test Procedure

The cement test is carried out as follows:

1. Prepare necessary reagents.
    - a. Tap water.
    - b. Nitric acid solution (5 percent).
    - c. EGTA solution.
    - d. Potassium hydroxide solution (1.0 N KOH).

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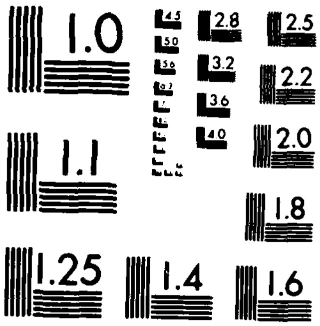

MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

e. Calcium standard solution (10 mg %).

f. Calcein indicator solution.

2. Prepare washing machine for testing.

a. Fill the washing machine with 10 gal (37.6 L) of tap water to the fill mark on the side of the tank. The tap water used to fill the tank should come from the same source as that used to prepare the calibration curve and that used to make the concrete.

b. Place nested sieves (No. 4 and No. 50) on the washing machine.

3. Prepare the calcium analyzer for testing. The calcium analyzer instruction manual gives simple and direct instructions for operation and maintenance should any difficulties occur. The instruction manual should be read thoroughly before operation.

a. Push the power button; a light will indicate that the power is on. Allow the analyzer to warm up for at least 15 minutes.

b. Check optical light positioning, install EGTA solution in side compartment of analyzer, and purge the system per instruction manual, i.e., remove all air from the titrating system.

The optical light positioning should remain stable once set. Each bottle of EGTA solution is enough for about 700 determinations, and the system need only be purged after a new bottle of EGTA solution is installed.

4. Calibrate the calcium analyzer (daily operation). Each time a cuvette with fresh reagents is prepared, it should be standardized and calibrated against a standard solution of calcium (10 mg %). When two successive calibration titrations agree within stated limits, the operator enters the information into the memory banks by pushing the calibration button. If the instrument has been turned off or has not been used for some time, it must be recalibrated. The care exercised in the calibration procedures will be reflected in the accuracy of the results. To calibrate:

a. Push the power button, which will light to indicate the power is on, and allow the instrument to warm up for at least 15 minutes.

b. Set toggle switch to "mg%." The toggle switch should remain on "mg%" for all testing.

c. Push the test light control directly above the power button to illuminate displays and buttons. The digital readout display should show a series of 8's. This confirms the operation of all safety lights and assures that all the segments of the digital readout are operating. Failure of the digital readout display to pass this test indicates that the system is defective and must be serviced.

d. Partially lift the cuvette door and inspect the light being emitted from the source lamp. The operator should see the white light coming directly from the source lamp at the extreme rear of the compartment. This light then passes through the optical filters and enters the cuvette as a blue light.

e. Lift the cuvette door and insert an empty, but wet, cuvette into the well. Check to see that the stirring magnet is operating.

f. Fill the cuvette to the etched line with 1 N KOH solution (about 12 ml) and add 100 µl (eppendorf pipet) of the calcein indicator solution. Insert the cuvette into the instrument.

g. Add 100 µl of the calcium standard to the cuvette.

h. Partially close the cuvette door and observe the source light entering the cuvette. The fluorescence in the cuvette should appear greenish in color. After fluorescence in the cuvette has been assured, completely close the door to the cuvette compartment.

i. Push the titrate button, which will begin to flash. No numbers will appear on the digital readout display during this conditioning cycle. The cuvette door must remain closed during all titrations.

j. Leave the cuvette in the analyzer and add 100 µl of calcium standard. Close the door and push the titrate button. When the ready light comes on, record the calcium content of the sample which appears on the digital readout display.

k. Leaving the cuvette in the analyzer, add another 100-µl sample of calcium standard and titrate. Record the result and compare it with that of the previous determination. Continue repeating until consecutive results are less than 0.15 units apart. When two consecutive results agree within the stated limit, push the calibration button. This button will light momentarily, indicating that the calcium analyzer has been calibrated.

l. Run an additional 100-µl sample of the calcium standard to ensure that the calcium standard readout value is 10.0 ± 0.15 mg %. The analyzer is now ready for testing.

m. About once a week, inspect the connecting tubing leading from the top of the solenoid valve to the cuvette for the presence of air bubbles. Small bubbles will not affect the operation of the analyzer, but these may possibly accumulate to a size sufficient to completely block the tubing. These large bubbles should be removed by (1) preparing a cuvette for the normal calibration procedure (Steps 4f through 4i), adding 1 ml of the calcium standard, and titrating. During the titration, manually manipulate the tubing so air bubbles discharge into the cuvette. This process can be expedited more efficiently by closing off the glass tube to the EGTA bottle with a finger and lightly squeezing the EGTA bottle.

5. Obtain a 2-kg ± 200 g sample of fresh concrete in a 0.5 gal polyethylene wide-mouth jar and record the mass to the nearest gram. The sample of concrete from which the cement content test specimen is made must be representative of the entire batch. The sample should be well mixed to ensure homogeneity.

6. Transfer the test specimen to the sieves nested over the washing machine and turn on the recirculating pump and agitator. Wash the residue from the sample into the tank using the jet of water from the recirculating pump hose. Keep jet of water moving slowly over the surface of the sieve to avoid loss of suspension by splashing.

a. Be sure to remove all material from the sample container onto the sieves nested over the washing machine.

b. Wash the plus No. 4 material carefully, using the jet of water from the recirculating pump hose. After all the minus No. 4 material has been washed through the sieve (normally requiring 1 to 1.5 minutes), remove the No. 4 sieve and its contents.

c. Wash the plus No. 50 material carefully, using the jet of water from the recirculating pump hose. After all the minus No. 50 material has been washed through the sieve (normally requiring 1 to 1.5 minutes), remove the No. 50 sieve and its contents.

7. After washing the sample through the sieves, obtain a representative sample (30 ml) of the suspension in the tank by using a 30-ml syringe pipet. The syringe pipet, because of the abrasive action of the particles, will become inaccurate after a period of time and must be replaced.

8. Drain the 30-ml sample from the syringe pipet into an Erlenmyer flask of at least a 500-ml capacity with a Teflon-coated magnetic stirring rod.

9. Refill the syringe pipet with 30 ml of 5 percent nitric acid solution and add the acid solution to the contents of the flask. While discharging the acid solution from the syringe pipet, occasionally shake it to ensure that all cement that settled out when the cement sample was obtained has dissolved and is flushed out with the acid solution.

10. Add 250 ml of tap water from a volumetric flask to the Erlenmyer flask.

11. Turn on magnetic stirrer and stir the solution in the Erlenmyer flask for 3 minutes to ensure a homogeneous solution.

12. Make sure that the cuvette has been filled with 1 N KOH solution to the fill mark, that 100 μl of the calcein indicator solution has been added, and that the instrument has been calibrated to accept 100-μl samples. Samples of unknown calcium content may be analyzed sequentially in the same cuvette that was prepared and used for the analyzer calibration. The empty cuvette light will begin to flash when the cuvette is full. If the instrument has not been used recently, verify that it is properly calibrated by testing 100-ul samples of the calcium standard solution before testing the actual sample. If the instrument calibration has drifted, it will be necessary to recalibrate (Steps 4b through 4l).

13. The relative calcium concentration of the solution in the 500-ml flask is determined by the calcium analyzer.

a. Withdraw a 20-µl sample of the unknown from the flask, while stirring continues, using a 20-µl eppendorf pipet.

b. Drain the 20-µl sample into the cuvette and close the door.

c. Push the titrate button, and wait for the completion of the titration. When the ready light comes on, record the value from the digital readout display and proceed with the next sample.

d. Repeat Steps 13a through 13c until values are less than 0.15 units apart and record the results. Use an average of all numbers that are within 0.15 units of each other to determine the relative calcium concentration.

14. The cement content of the sample in grams can now be estimated by referring to a previously established calibration curve for the cement type and materials being used.

15. Empty and clean washing machine for next test.

Calibration Requirements

The calibration curve for determination of cement content is established by performing a standard cement test on two prepared samples. The zero cement sample is prepared by using the materials and mix proportions of the concrete to be tested to make a 2-kg sample, minus the cement and its respective weight. The calibration sample is a 2-kg sample prepared using the materials and mix proportions of the concrete to be tested, including the cement. A calcium titration (calcium analyzer) is performed on the zero cement sample and the calibration sample. The results represent zero grams of cement and the mass of cement in the calibration sample, respectively. A calibration curve is then constructed. All unknown cement contents are lineraly proportional.

It is recommended that new calibration data be established whenever: (1) the cement source or type used to produce the concrete is changed or on a weekly basis if the cement source or type do not change, (2) the aggregate source is changed, (3) the design mix is changed, and (4) the strength of the reagents are changed or the reagent expiration date is reached.

The zero cement calibration is carried out as follows:

1. Prepare necessary reagents as in step 1 of the cement test procedure.

2. Prepare calcium analyzer as in step 3 of the cement test procedure.

3. Calibrate the calcium analyzer to accept 100-µl samples as in step 4 of the cement test procedure.

4. Prepare a 2-kg ± 200 g minus cement sample using the raw materials in the same proportions and from the same source as that used to produce the concrete being tested.

5. Follow Steps 6 through 13 of the cement test procedure, except use a 100-μl sample in Step 13 instead of a 20-μl sample. The relative calcium concentration of the "zero cement" sample represents one point on the calibration curve.

The concrete calibration sample is tested as follows:

1. Prepare necessary reagents as described in Step 1 of the cement test procedure. Also hand mix a 2-kg concrete calibration sample using the materials and mix proportions of the concrete to be tested. The materials used to prepare the calibration sample must come from the same source as that used to produce the concrete being tested.

2. Prepare the washing machine and calcium analyzer for testing as described in Steps 2 and 3 of the cement test procedure.

3. Calibrate the calcium analyzer to accept 100-μl samples as described in Step 4 of the cement test procedure.

4. Follow Steps 6 through 13 of the cement test procedure. Repeat Steps 7 through 13 of the cement test procedure, as necessary, to verify that a representative subsample was obtained. The relative calcium concentration of the calibration sample represents the mass of cement in the calibration sample and gives another point on the calibration curve.

5. To construct the linear calibration curve of cement content in grams vs calcium analyzer reading (mg %), plot 0 g of cement and the "zero cement" calibration result divided by 5 and plot the mass of cement in the 2-kg concrete calibration sample and its corresponding calcium analyzer reading. Connect the two points to complete the calibration curve. All unknown cement contents are linearly proportional.

6. Since the calibration curve is a straight line determined by two points, a linear equation can be developed as follows:

$$\text{Cement content (gram) } y = \left(X - \frac{T}{5}\right)\left(\frac{W}{S - \frac{T}{5}}\right) \qquad \text{[Eq C1]}$$

where:

y = cement content of sample in grams

X = calcium analyzer reading for sample

W = mass of cement in the 2-kg concrete calibration sample (in grams)

T = calcium analyzer reading for "zero cement" calibration

S = calcium analyzer reading for the 2-kg concrete calibration sample.

The cement content can be stated as a percentage by dividing the predicted value by the mass of the sample tested and multiplying the result by 100.

Water Test

Reagents

The reagents required for conducting the water content test are:

1. Distilled water. Distilled water is used to dilute the blank necessary for determining chlorides in the concrete.

2. Tap water. Tap water is needed to make the sodium chloride solution.

3. Sodium chloride solution (0.5 N). Obtain 292.2 g of dry sodium chloride (NaCl) and dissolve in tap water. Finish by adding tap water until 10 L of solution are obtained. Since dry NaCl crystals dissolve slowly, it is recommended that mechanical agitation be used to ensure that the NaCl crystals are completely dissolved.

4. Acid buffer solution. This solution provides the medium in which the coulometric titrations of chloride are performed. Each bottle contains the following ingredients: polyvinylalcohol (0.9 g/100 ml); glacial acetic acid (4.8 g/100 ml); nitric acid (0.16 g/100 ml); NaCl (4 g/100 ml); deionized water. The reagent should be stored at room temperature (18° to $25^\circ C$). Avoid contact with eyes and skin. If contacted, flush thoroughly with water.

5. Chloride standard solution (100 mEq/L). This solution is used for calibrating the chloride meter. This reagent should be stored at room temperature (18° to $25^\circ C$).

6. Silver electrode polish.

Reagents 4 through 6 are available in prepackaged form from the manufacturer of the chloride meter.

Water Test Procedure

The water content test is carried out as follows:

1. Prepare necessary reagents:

    a. Distilled water.

    b. Sodium chloride solution (0.5 N).

    c. Acid buffer solution.

    d. Chloride standard solution.

    e. Silver electrode polish.

2. Prepare chloride meter for testing. The chloride meter instruction manual gives simple and direct instructions for operation and maintenance should any difficulties occur. The instruction manual should be read thoroughly before operation.

a. Push the power switch to the "on" position and the digital display will illuminate.

b. Move the sample selector switch to the 100-μl position. All readings should be taken with the sample selector switch in this position.

c. Remove the two rear and right-front silver electrodes, clean with silver electrode polish, and reinstall them in the meter. These electrodes should be removed and cleaned each time a fresh acid buffer solution is used. The front-left electrode should be replaced as necessary.

d. Fill the 20-ml beaker with 15 to 17 ml of acid buffer solution. The volume is not critical and can be estimated by the gradations on the beaker.

e. Place the 20-ml beaker containing the acid buffer solution on the platform. Lower the electrodes into the solution and depress the condition switch. The conditioning cycle display will illuminate. This cycle conditions the acid buffer solution, and the reading at the end of the cycle should be disregarded. This step must be performed each time a fresh acid buffer solution is used.

f. When the conditioning cycle is completed, add 20 μl (Eppendorf pipet) of the chloride standard to the beaker of acid buffer solution without removing the electrodes, depress the titrate button, and record results. Repeat as necessary to ensure reproducibility. The theoretical reading is 20 mEq/L.

g. The chloride meter is ready for testing after it has been properly calibrated. Samples of unknown chloride concentration may be analyzed sequentially in the same beaker prepared and used to condition the meter. To analyze a sample: (1) pipet the sample into beaker containing acid buffer solution, (2) depress the titrate button, and (3) record the result directly in milliequivalents per liter of chloride. This procedure may be repeated until the change solution light appears.

3. Condition the chloride meter, Steps 2a through 2f, and determine the chloride concentration of the 0.5 N (500 mEq/L) NaCl solution by placing a 100-μl sample into the 20-ml beaker containing the acid buffer solution. Lower the electrodes, press the titrate button, and record the result in milliequivalents per liter. Repeat using a new 100-μl sample, as necessary, to ensure reproducibility. Use an average of all numbers to within ±4 mEq/L.

4. Obtain two 2-kg ± 200 g samples of fresh concrete. Place each in a separate 0.5 gal polyethylene wide-mouth jar and record the mass to the nearest gram. The sample of concrete from which the water content test specimens are made must be representative of the entire batch. The sample should be well mixed to ensure homogeneity.

5. Using a volumetric flask, add 250 ml of 0.5 N sodium chloride solution to one jar. This is the sample required for estimating the water content of the concrete. Add 250 ml of distilled water to the other jar. This is the blank required for estimating chlorides in the concrete itself.

If the concrete being tested does not contain chlorides, use of the blank may be discontinued after the initial determination.

6. Secure watertight lids on both containers.

7. Turn the two jars end-over-end in a 40- to 60-rpm mixer, or by hand for at least 3 minutes. The jars should never be turned so rapidly that centrifugal forces exceed gravitational forces, thereby inhibiting the complete intermixing of the salt solution (sample) and distilled water (blank) with the concrete samples.

8. Remove the jars from the mixer and loosen the lids. Transfer about 12 ml of the intermixed salt solution cement slurry (sample) to a 15-ml disposable test tube. Transfer about 12 ml of the intermixed distilled water cement slurry (blank) to a 15-ml disposable test tube.

9. Place tubes in opposite positions in the centrifuge and centrifuge at 2000 and 3000 rpm for 30 to 60 seconds. The tubes should be clearly marked so that they can be properly identified after the centrifuge operation.

10. Remove the tubes from the centrifuge and use a small spoon to wipe out any foam that has accumulated on top and recentrifuge the sample and blank for 30 to 60 seconds.

11. Make sure the chloride meter has been properly calibrated to accept 100-µl samples and that the acid buffer solution has been properly conditioned (Steps 2a through 2f).

12. Use the chloride meter to determine the chloride concentration of the sample and blank solutions in the test tubes.

a. Sample. Withdraw 100 µl of the salt solution cement slurry from the sample tube and place into the 20-ml beaker containing the acid buffer solutions. Lower electrodes, press the titrate button, and record the result in milliequivalents per liter. Repeat using a new 100-µl sample, as necessary, to ensure reproducibility. Use an average of all numbers to within ±4 mEq/L.

b. Blank. Withdraw 100 µl of the distilled water cement slurry from the blank tube and analyze as described in Step 12a. If the concrete being tested does not contain chlorides (chloride strength of blank equal to zero), use of the blank test results can be discontinued after the initial determination.

13. The water content of an unknown sample is calculated as follows:

$$\text{Water content (grams)},\ y = 250\left(\frac{\text{NaCl}}{\text{Sample} - \frac{\text{Mass sample}}{\text{Mass blank}}\ (\text{Blank})} - 1\right) \qquad [\text{Eq C2}]$$

where:

y = water content of sample in grams

NaCl = NaCl chloride concentration in milliequivalents per liter

Sample = sample chloride concentration in milliequivalents per liter

Blank = blank chloride concentration in milliequivalents per liter

Mass sample = mass of sample in grams

Mass blank = mass of blank in grams.

The computed water content represents the amount of free water in the original specimen tested. The computed water content is in grams. The computed water content may be stated as a percent of the total specimen weight by dividing the computed water content by the mass of the concrete test specimen and multiplying the result by 100.

APPENDIX D:

MATERIAL CHARACTERISTICS

Table D1

Coarse Aggregate

Type: No. 57 Limestone (Crushed Limestone)		Type: Ohio River Gravel	
Source: Construction Materials, Inc. Morgantown, WV		Source: Dravo Corporation Neville Island, PA	
Gradation		Gradation	
Sieve Size	Percent Passing	Sieve Size	Percent Passing
1 in. (25.0 mm)	100	1 in. (25.0 mm)	100
3/4 in. (19.0 mm)	91	3/4 in. (19.0 mm)	95
3/8 in. (9.5 mm)	18	3/8 in. (9.5 mm)	43
No. 4 (4.75 mm)	1.0	No. 4 (4.75 mm)	4
No. 8 (2.36 mm)	0.8	No. 8 (2.36 mm)	1.4
No. 16 (1.18 mm)	0.7	No. 16 (1.18 mm)	1.1
No. 30 (600 μm)	0.7	No. 30 (600 μm)	1.0
No. 50 (300 μm)	0.5	No. 50 (300 μm)	0.7
No. 100 (150 μm)	0.5	No. 100 (150 μm)	0.4
No. 200 (75 μm)	0.4	No. 200 (75 μm)	0.2
Fineness modulus = 6.9		Fineness modulus = 6.5	
Specific Gravity		Specific Gravity	
Apparent Sp. Gr. -	2.73	Apparent Sp. Gr. -	2.67
Bulk Sp. Gr. -	2.68	Bulk Sp. Gr. -	2.51
Bulk Sp. Gr. (SSD) -	2.69	Bulk Sp. Gr. (SSD) -	2.57
Absorption, percent -	0.75	Absorption, percent -	2.31

Table D2

Fine Aggregate

Type: Ohio River Sand

Source: Construction Materials, Inc.
Morgantown, WV

Gradation

Sieve Size	Percent Passing
3/8 in. (9.5 mm)	100
No. 4 (4.75 mm)	98
No. 8 (2.36 mm)	78
No. 16 (1.18 mm)	63
No. 30 (600 μm)	46
No. 50 (300 μm)	16
No. 100 (150 μm)	4
No. 200 (75 μm)	1.5

Fineness modulus = 2.9

Specific Gravity

Apparent Specific Gravity	2.67
Bulk Specific Gravity	2.58
Bulk Specific Gravity (SSD)	2.62
Absorption (percent)	1.30

Daravair-R Air-Entraining Admixture*

Daravair, an air-entraining admixture manufacturered by the Construction Products Division, W. R. Grace and Co., is an aqueous solution of Vinsol resin that has been neutralized with sodium hydroxide. The ratio of sodium hydroxide to Vinsol resin is one part of sodium hydroxide to 6.9 parts of Vinsol

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*Information supplied by Construction Materials, Inc., Morgantown, WV.

resin. The percentage of solids based on the residue resulting from evaporation and subsequent drying at 104°C is 19 to 22 percent. No other additive or chemical is present in this solution. Daravair contains no volatile flammable ingredients. It freezes at -2.8°C, but its air-entraining properties are completely restored by thawing and thorough stirring. Daravair is formulated to comply with specifications for Air-Entraining Admixtures for Concrete, American Association of State Highway and Transportation Officials (AASHTO) Designation M-154, and meets West Virginia state specifications.

There is no standard addition rate for Daravair. Under normal concreting conditions, Daravair at the rate of 0.75 to 3 fluid oz per sack of cement will provide sufficient air in the concrete.

APPENDIX E:

ADMIXTURE CHARACTERISTICS PROVIDED BY MANUFACTURERS

Daravair-R

Manufacturer: Construction Products Division, W. R. Grace and Co.

Description: An air-entraining admixture for concrete. It is an aqueous solution of Vinsol resin that has been neutralized with sodium hydroxide. The ratio of sodium hydroxide to Vinsol resin is one part of sodium hydroxide to 6.9 parts of Vinsol resin. The percentage of solids based on the residue resulting from evaporation and subsequent drying at 220^{o}F (378^{o}K) is 19 to 22. No other additive or chemical is present in this solution. It contains no volatile flammable ingredients. It freezes at 27^{o}F (270^{o}K), but its air-entraining properties are completely restored by thawing and thorough stirring. Daravair is formulated to comply with specifications for Air-Entraining Admixtures, AASHTO.

Designation: M-154.

Recommended dosage: Three-quarters to 3 fluid ounces (0.023 to 0.09 L) per sack of cement. Daravair is fully effective in concrete containing other admixtures and initial set retarders. Each material, however, should be added to the concrete separately.

Sikament (*Sikamix 126*)

Manufacturer: Sika Chemical Corporation.

Description: A super water-reducing admixture for concrete. Formulated with a powerful dispersing agent, it separates cement particles in low-water mixes to provide low-slump concretes. Sikament is free of calcium chloride and may be used in all concrete. The specific gravity is 1.2 and pH is 8.0.

Recommended dosage: Twelve to 36 fluid ounces (0.36 to 1.08 L) per sack of cement. The higher the dosage, the faster the strength gain and the more plastic the mix. For best results, add to mix a maximum of 60 minutes before placement. Add manually or by dispenser into the sand or water.

Lubricon R

Manufacturer: American Admixtures and Chemicals Corporation.

Description: A set-retarding, water-reducing admixture for concrete. Conforms to ASTM C-494, Type B and D, when used at recommended dosage. Contains no calcium chloride.

Recommended dosage: Four to 6 fluid ounces per 100 lb (0.12 to 0.18 L per 45 kg) of cementitious material. Dosage may be increased if additional retardation is required.

Lubricon Rapid Set

Manufacturer: American Admixtures and Chemicals Corporation.

Description: A water-reducing, accelerating admixture for concrete. Conforms to ASTM C-494, Type E, when used at recommended dosage. Contains calcium chloride.

Recommended dosage: Sixteen to 32 fluid ounces per 100 lb (0.48 to 0.96 L per 45 kg) of cementitious material.

Plastiment (Sikamix 100)

Manufacturer: Sika Chemical Corporation.

Description: A nontoxic, noncorrosive, nonair-entraining, water-reducing retarder. The action of Plastiment is independent of the action of air-entraining agents, calcium chloride, fly ash, or similar admixtures. The active ingredient is a metallic salt of hydroxylated carboxylic acid. Plastiment is slightly alkaline.

Recommended dosage: Two fluid ounces (0.06 L) per sack of cement. Add to sand, gravel, stone, or water before mixing. For special conditions, proportions can be increased. Plastiment is designed for use with all portland cements and all types of aggregates. To maintain equal slump, reduce water 1-1/2 to 2 gal/cu yd (1.4 to 5.7 L/m^3) of concrete.

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