

# RESEARCH RESULTS DIGEST

September 1990

Number 174

These Digests are issued in the interest of providing an early awareness of the research results emanating from projects in the NCHRP. By making these results known as they are developed, it is hoped that the potential users of the research findings will be encouraged toward their early implementation in operating practices. Persons wanting to pursue the project subject matter in greater depth may do so through contact with the Cooperative Research Programs Staff, Transportation Research Board, 2101 Constitution Ave., N.W., Washington, D.C. 20418.

**Areas of Interest:** 32 cement and concrete,  
33 construction (01 highway transportation,  
02 public transportation, 03 rail transportation,  
04 air transportation)

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## Determinations of Water:Cement Ratio in Fresh Concrete

*An NCHRP digest of the essential findings from the agency final report on NCHRP  
Project 10-25A, "Instantaneous Determination of Water-Cement Ratio in Fresh  
Concrete," prepared by Wiss, Janney, Elstner Associates, Inc., Northbrook, Illinois*

### THE PROBLEM AND ITS SOLUTION

Concrete is unusual among construction materials in that it is manufactured as used and cannot be tested for acceptance in advance. Because it gains strength over a long period of time and the level of strength assumed in design may vary from that attained in a period ranging from one day to three months, acceptance is commonly based on strength tests at an advanced age. There is, therefore, at any given time, a large amount of concrete in-place, on most projects, the acceptability of which has not been determined. Clearly, a need exists to assess the quality of concrete much earlier, ideally before it is placed.

It is generally agreed that knowledge of the water:cement ratio of concrete at a given air content provides a highway engineer with a major measure of its quality. Unfortunately, design of quality concrete does not ensure that such concrete is placed in the structure. The concrete may be misbatched; aggregates may contain excessive water; fly ash may be mistaken or substituted for cement; extra water may be introduced as wash-water in the mixing truck or by the truck driver as the mix stiffens. Thus, knowledge of the water: cement ratio (and the air content) of the concrete actually delivered to the job is of paramount importance.

NCHRP Project 10-25A was initiated in response to this need. The objective of the research was to develop a method of measuring the water:cement ratio in concrete that could form the basis of an acceptance test at the job site. The desirable characteristics required of such a method are: (1) rapidity -- results should be obtainable within 2 min or less; (2) accuracy -- measurement of water:cement ratio to within 0.02; (3) cost -- the equipment should be of such price (under \$5,000) that a testing agency might reasonably be expected to acquire several items, (4) convenience -- the method should consist of a probe to be inserted directly into a central or truckmixer, (5) versatility -- the test should be capable of being performed at any time from first mixing up to the maximum delivery time allowable (approximately 90 min at a concrete temperature of 70°F), and (6) simplicity -- the probe should be easily calibrated so that the effects of changing concrete material and temperature may be accommodated.

### FINDINGS

It has been well established that the quality of concrete, primarily as measured by its strength, is largely an inverse function of its water:cement ratio -- the ratio of the net weight of water in the mix (the

water in excess of that required to saturate the aggregates) to the weight of cement. To date, there has been no method of determining the water:cement ratio of fresh concrete that has had broad acceptance. The published methods are generally too slow (15 min to 30 min, or more), too inaccurate, or too subject to interference for acceptance purposes. Indeed, most of the methods that have had even limited acceptance are for cement content and not for water:cement ratio.

In the last several years, enormous strides have been made in the development of "specific ion" or "ion-selective" electrodes that measure the concentration of an ion (or a gas) in a water solution. The first specific ion electrode was developed over 50 years ago and measured the concentration of hydrogen ion ( $H^+$ ); the instrumentation developed was the familiar pH meter. More recently, electrodes have been developed that measure the concentration of many other types of ions (and some gases) in solution. Among these ions are sodium ( $Na^+$ ), potassium ( $K^+$ ), chloride ( $Cl^-$ ), and bromide ( $Br^-$ ).

The development of such electrodes led to the present study (NCHRP Project 10-25A). In theory, if any ionic species in portland cement is completely soluble in water, a measure of its concentration in the aqueous phase of fresh concrete could uniquely provide the water:cement ratio of fresh concrete. The major initial experimental work for Project 10-25A involved the search for suitable ions in cement and for the instrumentation to measure their concentration.

An extensive literature search was made to determine what analytical procedures and instrumentation had been, or could be, used to determine the water:cement ratio of fresh concrete. The prime consideration was for a procedure that would employ a "probe" that could be inserted into fresh concrete and directly read out the water:cement ratio. However, separate rapid methods for water and cement were also sought, as was information that would provide guidance in the incorporation of a "tracer" into portland cement so that the tracer's concentration, and thus the amount of cement in a concrete mix, could be determined.

The search did not reveal any successful development of a probe, but did suggest the use of a specific ion electrode that would selectively determine the concentration of a water-soluble constituent of the portland cement in the mix water of the concrete. If the concentration of such a constituent varies with water content in a predictable way (e.g., through calibration), a single measurement would relate to water:cement ratio.

Analyses for water-soluble constituents of cement disclosed that only a few were candidates for the program, with sodium and potassium ions the ones of choice. Using commercial electrodes it was found that for simple water plus cement mixes, the concentration of sodium and potassium varied with time, water:cement ratio, and cement source. Calibration was found to permit water-cement determinations for a particular cement in a simple cement-water system.

As the system became more complex, e.g., when aggregate was introduced and when measurements were made over a period of an hour or more, many

complications were introduced, including nonreproducibility of the electrode due to "poisoning" by the concrete fines and solutions; change in the solubility of the measured ions with time; and loss of mix water due to reaction with the cement. Prototype electrodes were manufactured in an attempt to obviate the first of these complications but without complete success.

After extensive efforts, the specific ion electrode approach was abandoned, but the work should be of great value in allowing successful analyses in the future when the electrode technology advances, or when additional experiments are performed to allow a better understanding of the solution chemistry of cement systems. The electrodes now available can greatly aid in the latter experiments.

Simultaneous with the above effort, several other approaches to the water:cement ratio determination were investigated. None allowed a single-probe measurement of water:cement ratio, but two methods for water and one for cement appeared to offer promise. They were developed to the stage where each appears to be equal to or better than any others now available; a brief description of each method follows:

1. A cement content procedure employing a colorimetric method to determine silica content of cement. The method was a modification of one used for rapid analyses of cements. The researchers found that the original method could be shortened considerably and adapted to large concentrations of silica in concrete. As developed, the procedure allows an 8 - min to 10 - min determination of cement content, without necessity for an electrical power source. A waiting time in the procedure allows the operator to simultaneously determine water content. Interferences to the method are few. However, some aggregates and fly ashes will cause interferences. For a well-controlled mix, calibration for these interferences will eliminate such interference errors.

2. A water content procedure employing a microwave oven to determine moisture content of samples. A special ashing block assembly allows a determination of water-loss in about a minute, in marked contrast to the 15 - min to 60 - min required by other published procedures. The success of this method lies in the fact that it is quick, accurate, and economical. One drawback to the microwave oven is that it requires a power source.

3. A water content procedure employing a bromide solution addition to the concrete sample to determine the amount of dilution by the mix water. This procedure has not been fully developed, but the rapid, reasonably accurate analyses now possible suggest that the method could replace the present procedure of the Kelly-Vail method that is the basis of the U.S. Army Corps of Engineers and ASTM procedures. The present Kelly-Vail water method requires considerable expertise and instrumentation, and any chloride in the concrete mix causes interference.

As developed, and if a power source is available, a combination of the silica procedure and the microwave water determination may surpass any other published

methods in speed, accuracy, and freedom from interference.

A separate phase of the study involved a search for a "tracer" element or substance that could be added to portland cement during its manufacture which would permit analyses for cement content through determination of its concentration, or directly for water:cement ratio if it were soluble in water. Because attention centered on substances that were detectable by specific ion electrode, this study was largely abandoned when the specific ion electrode work was stopped. However, the efforts did suggest that nitrate and bromide would be candidates for such a tracer.

The results of the studies of Project 10-25A did not meet the aspirations of the contract proposal, which was a research project with a prescribed goal to develop a single electronic probe for directly measuring the water:cement content in fresh concrete. The goal was not met primarily because specific ion technology and instrumentation were not yet developed to the extent necessary for the severe requirements of the project.

The project did develop: a cement content procedure that is probably the fastest generally applicable one now available; a water content procedure that is probably an order of magnitude faster than almost any other published procedures; and specific ion procedures that can provide important applicability to early cement chemistry.

The project also identified other published procedures that may have applicability to cement content analyses under specific circumstances.

## CONCLUSIONS

The project disclosed many areas of research that should prove fruitful in the fields of highway engineering and general construction, which were not carried out because of time, money or limitations imposed by program requirements. These areas are discussed below.

### Specific Ion Technology

The developments in specific ion electrode construction during Project 10-25A should provide a basis for improvements by specific ion electrode manufacturers. The work disclosed that the electrodes could perform well in simple dilute cement and water systems, but performance degraded in more concentrated pastes or in mortars and concretes. Back-flow and reference solution contamination were identified as problem areas which probably could be overcome by design changes.

Double or multiple measurements of electrode potential may also improve the water:cement ratio or water-content determination. In this procedure the electrode potential is read out not only on the concrete sample to be tested but also on a well-defined control concrete specimen, and the difference between the two read-outs is correlated with the difference between the water:cement ratio (or water content) of the sample

and that of the control.

The applicability of specific ion technology to systems was demonstrated and could be extended to other ions; to the determination of ion concentrations as a function of variables such as admixture type and, dosage, temperature, and aggregate type (e.g. calcareous vs. siliceous); and to the development of relationships between early chemistry and concrete strength, volume stability, and workability.

### Cement Content Procedure

The developed colorimetric procedure was found to be fast and accurate for mortars and concrete. Further work should be performed to make the procedure more applicable to technician or laborer use in the field and to determine degree of interference by aggregates and admixtures not investigated.

### Water Content Procedures

Although the microwave procedure employing the special holder is so fast that significant improvements in that regard appear unlikely, experimentation to make the method applicable to larger samples and to make the equipment more field worthy (e.g., portable, battery-driven, and inexpensive) would appear to offer promise.

Less expensive suction filtration and acetone drying procedures should be developed further as a back-up where rapid, inexpensive instrumentation is required in remote field locations.

### Sampling Procedure

The sampling procedure developed for this test has been found applicable to samples of about a cubic yard. Application to ready-mix trucks has not been attempted, but experimentation in this area is a necessity. Obviously, the method has immediate applicability to mixer efficiency testing, but it is not known if samples taken from the top (or middle or bottom) of the ready-mix truck or central mixer will be representative of the entire mix, or if samples from several areas of the mixer must be combined.

## FINAL REPORT

The agency final report, entitled "Instantaneous Determination of Water:Cement Ratio in Fresh Concrete," gives a detailed account of the conduct of the research, the findings, interpretations, applications, and conclusions. Tables, graphs, cited references, and a comprehensive bibliography of published materials having value in fresh concrete chemistry and analysis work are included.

The agency final report is available for loan or purchase (\$15.00) on request to the National Cooperative Highway Research Program, Transportation Research Board, 2101 Constitution Avenue, N.W., Washington, D.C. 20418.

### **ACKNOWLEDGMENTS**

The research project summarized herein was performed under NCHRP Project 10-25A by Wiss, Janney, Elstner Associates, Inc. (WJE). William G. Hime, Principal, was Principal Investigator and wrote a major portion of the agency report. Ms. Bernie K. Buttke provided major support in the report preparations.

Work at WJE was under the direction of Mr. Hime and was primarily performed by: Dr. Stella Marusin, Consultant, Co-Principal Engineer; James Connolly, Senior Consultant; Zvonimir Jugovic, Charles Weise, and Lee Petry, Consultants; and Robert Landgren, Senior Engineer.

Dr. James Ross, Vice President, and John Synnott, Director, of Orion Research, Cambridge, Massachusetts, were Co-Principal Investigators and performed a literature search and extensive specific ion electrode research and development. Dr. Sandor Popovics of Optimum Engineering Research, Lansdowne, Pennsylvania, Co-Principal Investigator, provided guidance and literature search efforts.

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