

Measuring the Chloride Content of Concrete

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The deterioration of reinforced concrete due to the corrosion of the reinforcing bars may be expressed as the sum of three time events: time to initiation of corrosion, time to first spalling, and time to failure. Three corrosion processes have to be characterized to determine the corrosion state of the concrete within the three events. The three processes are the rate of chloride diffusion and present level of chloride contamination, rate of corrosion, and rate of maintenance activities from first spalling to failure. Thus, measuring the chloride content of concrete as a function of depth is critical to determining the chloride contamination state and the rate of chloride diffusion into concrete. The present standard methods are too arduous, time-consuming, and costly for use in the field and for measuring the chloride content of the relatively large number of samples needed to characterize the chloride contamination level of concrete bridges. The laboratory work in the development of a field-worthy method of measuring the chloride content of reinforced concrete structures was addressed in this study.

A literature review was performed, and four methods were selected for the laboratory study: Quantab chloride titrator strips, specific chloride ion electrode, spectrophotometer, and argentometric digital titrator. The laboratory study was composed of the determination of the accuracy of the method with respect to the AASHTO T-260 standard method and the effect of cement content and temperature. In addition to the control with no additional chlorides added to a concrete mixture, contamination levels of 0.2, 0.4, 0.8, 1.6, 3.2, 6.4, 8.6, 10.8 and 12.8 lb chlorides/yd³ of concrete were tested. On the basis of accuracy, cost, speed, and level of expertise required, the specific ion electrode was selected for further evaluation of the effects of cement content and temperature. Cement content was shown to have no effect on the results. However, the reaction temperature does influence the measured chloride content. A correction factor was developed for the effect of the reaction temperature.

The deterioration of concrete bridges from the chloride-induced corrosion of the reinforcing steel in the United States is well known. A recent projection estimated the financial liability of corrosion-induced deterioration in bridges at \$20 billion, increasing at a rate of \$0.5 billion annually (1). To optimize the cost-effective solution to the protection, repair, and rehabilitation of concrete bridges, one must identify the present corrosion state of the bridge components. The corrosion state of a bridge component will be within one of the

three time events: time to initiation of corrosion, time to first spalling, or time to failure. The three processes associated with the time events are the rate of chloride diffusion and the present level of chloride contamination, the rate of corrosion, and rate of maintenance activities from first spalling to failure. Thus, measuring the chloride content of concrete as a function of depth is critical to identifying the present corrosion state and predicting the future contamination level using the rate of chloride diffusion.

The present standard methods of measuring the chloride content of concrete, AASHTO T-260 and ASTM C114, are too arduous, time-consuming, and costly for use in the field and for measuring the chloride content of the relatively large number of samples needed to characterize the chloride contamination state of concrete bridges. The laboratory work in the development of a field-worthy method of measuring the chloride content of reinforced concrete structures was addressed in this study.

BACKGROUND

Methods to use to determine the chloride ion content of concrete may be classified as nondestructive and destructive techniques. Nondestructive techniques include the dual neutron-gamma ray and the neutron-gamma ray spectroscopy. Destructive methods, requiring a drilled powdered sample, include the AASHTO standard method, x-ray fluorescence, gas chromatograph, Quantab chloride titrator strips, specific ion electrode, spectrophotometer, and argentometric digital titrator.

The dual neutron-gamma ray technique was developed for FHWA by Columbia Scientific Industries (2,3). The instrument is capable of measuring chloride content with respect to depth; its detection limits are 0.04 to 0.08 lb/yd³ and depth resolutions are 0.40 to 8 in., depending on the calibration model. The choice of the wrong calibration model (Cl⁻ depth distribution model) will result in significant measurement errors. Calibration models would have to be developed for specific types of bridges (e.g., concrete or steel beams, varying deck thickness, varying overlay thickness, coastal or inland bridges) (3). The method is relatively fast, 2 to 3 measurements per hour with a 10-min data acquisition time. Instrument operation is straightforward and requires little training. However, instrument calibration and setup must be done by qualified scientists. Although operational costs are relatively low, capital costs are high. Also, the equipment is large and is mounted on a self-contained vehicle and thus is limited to use on bridge decks.

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Neutron-gamma ray spectroscopy also uses a californium-252 neutron source for composition measurements, but uses a high-resolution, high purity germanium detector rather than a NaI (Tl) crystal gamma-ray detector (4–6). The instrument has been used to measure the relative difference with regard to surface position of the chloride content of a masonry wall by normalizing the chloride intensities to the value of silicon (Cl^-/Si ratio). The procedure assumes the value of silicon remains relatively constant throughout the material. Portability problems, calibration requirements, and equipment costs significantly limit the usefulness of the device for determining the chloride content of concrete bridge components.

X-ray fluorescence and gas chromatography analysis methods of powder samples offer no advantage over other powder analysis methods because of the related power requirements (x-ray fluorescence requires approximately a 100-kV source), cost (between \$25,000 and \$100,000 for equipment only), and level of expertise required. These limitations restrict the use of the instruments to the laboratory.

Quantab chloride titrator strips are simple and fast to use and are applicable to field measurement techniques of powder samples. Simplified procedures for the Quantab method were developed by the Building Research Station, Garston, Hartford, for analyzing the chloride content in portland cement concrete. The analysis procedure developed for the Quantab titrator strips consists of an acid digestion of a 5 g sample of powdered concrete. Fifty mL of 1 N nitric acid solution were used to digest the chloride followed by neutralization of the acid using 5 g of anhydrous sodium carbonate. Chloride concentration of the sample was then determined using the Quantab titrator strips (7).

The Building Research Station, Garston, Hartford, also developed a simplified procedure for the chloride determination in portland cement concrete using the (argentometric) test method. In this procedure, the 5-g powdered concrete sample is acid digested with 50 mL of 1 N nitric acid. While the sample mixture is being stirred, 5 g of sodium bicarbonate is added to the sample mixture. Once completely dissolved, the mixture is allowed to stand for 1 to 2 min. Finally, the mixture is filtered into a beaker using Whatman 41 or an equivalent filter paper. The filtered solution is then titrated by pouring 5.75 mL of the filtrate into a mixing bottle. One capsule of potassium chromate powder indicator is added to the sample. A silver nitrate solution is added drop by drop and the sample is swirled after each drop. The sample is titrated from a bright yellow to faint reddish brown color, and the number of digits required to complete the titration is recorded (7).

The development of the specific ion probe method for measuring the chloride content of concrete was first conducted at The Pennsylvania State University (8). The procedure was further developed for field use by James Instruments (9). The method digests a 3-g powdered sample in a chloride extraction solution. A combination specific chloride ion electrode connected to a voltmeter is inserted into the sample mixture, and the millivolt reading is recorded. The chloride content is determined by using a calibration equation, which in turn is determined every time the instrument is turned on.

The spectrophotometric method compares the color difference of a chloride extracted mixture with a standard reference solution. The chloride content is a direct digital readout in parts per million (10).

The most promising methods, on the basis of initial equipment cost, level of expertise required, and portability (which may be adapted to the rapid field measurement of the chloride content of reinforced concrete using powder samples), are the specific ion electrode, spectrophotometric, and argentometric digital titration methods, and Quantab titrator strips. Subsequently, these methods were selected for laboratory investigation.

EXPERIMENTS

The laboratory investigation of the four test methods consisted of three phases: accuracy of the four test methods as compared with the AASHTO standard test method, the effect of cement content, and temperature on the performance of a best select test method.

For the accuracy, cement content, and temperature tests, concrete specimens 1 ft² × 6 in. thick were cast at 10 chloride contamination levels. Specimens were cast at chloride additive rates of 0.0, 0.2, 0.4, 0.8, 1.6, 3.2, 6.4, 8.6, 10.8 and 12.8 lb Cl^-/yd^3 of concrete using a sodium chloride solution. Concrete slabs were cast at a water/cement ratio (w/c) of 0.40, 0.47, and 0.50 with Type I cement contents of 658, 640, and 552 lb/ yd^3 of concrete, respectively, at each of 10 chloride contamination levels. The fine aggregate was a natural sand and the coarse aggregate was a nominal 1-in. crushed limestone. The specimens were moist cured for 46 days. A rotary hammer drill with a $\frac{3}{4}$ -in. carbide drill bit was used to sample each of the concrete slabs. The extracted powder from the multiple drill holes in a single contaminated slab was combined, dried, and sieved over a number 50 sieve, and the retained 50 sieve material was discarded.

Bridge deck class concrete specimens (w/c = 0.47) were used in the initial series of chloride content tests to determine the accuracy of the four methods. The substructure and superstructure mixtures (w/c = 0.50 and 0.40, respectively) were used to determine the effects of cement content. A single chloride contamination level (1.4 lb Cl^-/yd^3) was used to determine the effects of chloride extraction reaction temperature.

LABORATORY TESTING

The standard potentiometric titration method was used to standardize the 0.01 N silver nitrate and sodium chloride solutions used for the analysis of chloride in accordance with the standard AASHTO procedure. Tests for chloride content using the four select methods were performed on standardized solutions to verify their accuracy before the specimens were tested. The test results for all four selected methods were within the range of accuracy specified by the manufacturers.

Specific Ion Probe

A deviation from the recommended calibration procedure involved a regression analysis of the calibration measurements instead of determination of the calibration equation graphically. This deviation was used to allow more precision in the test results.

A plot of the results obtained using the specific ion probe as a function of the potentiometric titration results and the 95 percent confidence limits for the prediction interval are presented in Figure 1.

Spectrophotometric

Samples analyzed using the spectrophotometer were also compared with the results obtained from the potentiometric titration procedure. A plot of the spectrophotometer and the potentiometric titration results and the 95 percent confidence limits for the prediction interval are presented in Figure 2.

Digital Titrator

Samples analyzed using the digital titrator were also compared with the results obtained from the potentiometric titration procedure. A plot of the digital titrator as a function of the potentiometric titration results and the associated 95 percent confidence limits are presented in Figure 3.

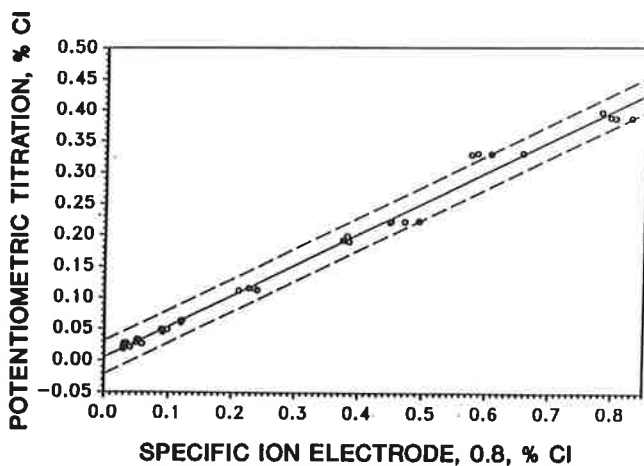


FIGURE 1 Potentiometric titration versus specific ion probe.

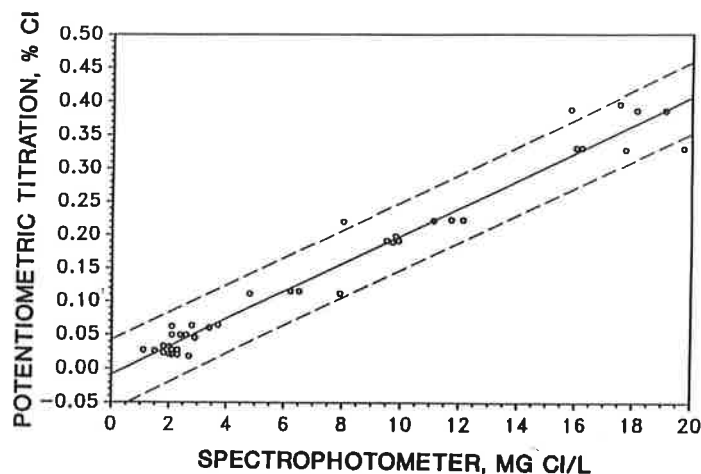


FIGURE 2 Potentiometric titration versus spectrophotometer.

Quantab Titrator Strips

Acid digested samples analyzed using the Quantab titrator strips were compared with the results obtained from the potentiometric titration procedure. A plot of the Quantab titrator strips number as a function of the potentiometric titration results and the 95 percent confidence limits for the predicted value are presented in Figure 4.

COMPARISON OF TEST METHODS

As indicated from an analysis of the results obtained from the first series of tests for chloride, the highest accuracy is achieved using the specific ion probe followed by the digital titrator, spectrophotometer, and the Quantab titrator strips (see Table 1). These are considered the most important criteria for selecting the appropriate method because errors in measuring the chloride content of bridges may influence the results obtained in estimating the extent of chloride contamination and in predicting the time to depassivation.

The initial cost of the specific ion probe was greater than the other selected methods. It should be noted that hidden costs are associated with the spectrophotometer, digital titrator, and the Quantab titrator strips. Items such as filter paper, beakers, stirring rods, nitric acid, and deionized water are required for all three methods. Additional items such as funnels, a funneling apparatus, and pipets are required for the spectrophotometer and the digital titrator. Finally, a magnetic stirrer and magnetic stirring rods are desirable when using the digital titrator.

No special sample preparation is required for the specific ion probe. The probe can be calibrated in less than 10 min, after which samples can be weighed and analyzed in less than 10 min. This allows the operator 7 min to weigh the sample before testing.

The procedure for weighing and preparing the sample for the spectrophotometer and the digital titrator requires the same amount of time. Once the samples are prepared, the analysis procedure using the spectrophotometer requires a little less than the digital titrator. The operator must pay

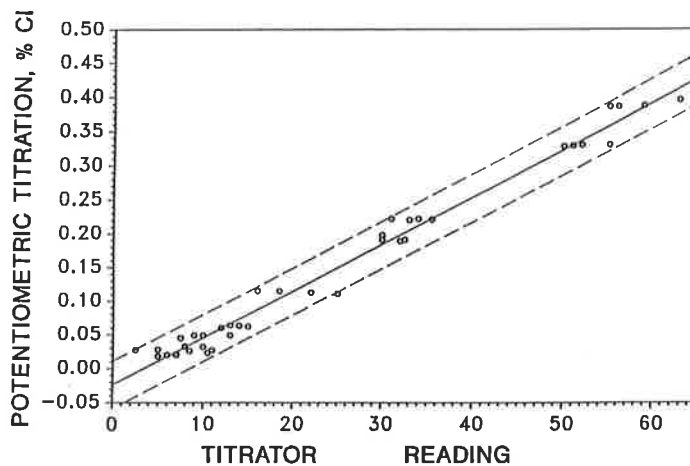


FIGURE 3 Potentiometric titration versus digital titrator.

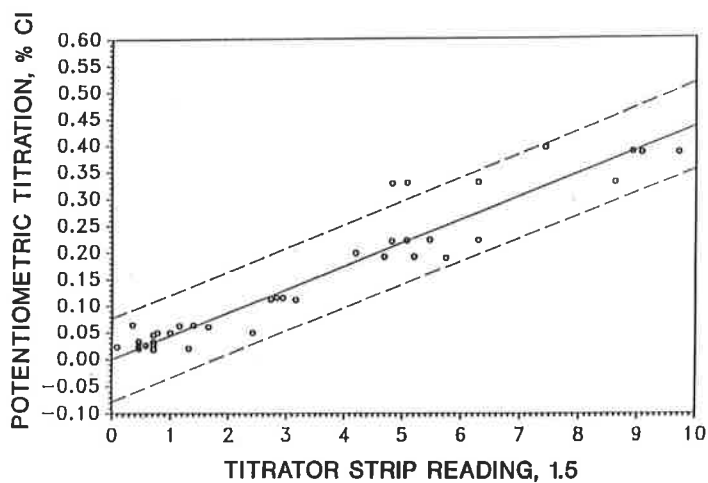


FIGURE 4 Potentiometric titration versus Quantab titrator strips.

TABLE 1 Comparison of Test Methods

Method	Accuracy R-sq (Adj)	*Cost	**Speed	*** Level of Expertise
Specific Ion Probe	99.0%	\$1860.90	1	Simple
Spectrophotometer	96.3%	1363.57	2	Medium
Digital Titrator	98.3%	156.74	3	Medium
Quantab Titrator Strips	91.2%	49.30	4	Simple

*Cost represents the initial cost of the equipment and the chemicals necessary for analyzing 40 specimens.

**Speed represents the order in which samples may be weighed, prepared, and tested using each method.

***Level of expertise gives an indication of how complicated each procedure is to use.

particular attention during the titrating procedure when using the digital titrator so the midpoint of the titration will be recognized.

The procedure for weighing and preparing the sample to be analyzed using the Quantab titrator strips does not require as much time as for the spectrophotometer and the digital titrator. However, sometimes the operator may be required to wait as long as 20 min before the results may be read using the Quantab titrator strips.

The analysis procedure for the specific ion probe was simplified for the operator when compared with the original procedure developed by James Instruments (9). Essentially, the operator records readings displayed by the electrometer while following a step-by-step procedure. Two precautions must be followed in using this procedure to obtain accurate results. Otherwise, the procedure is simple, quick, and straightforward. Procedures for the spectrophotometer and the digital titrator are a little more complicated than those for the specific ion probe. The operator not only must realize the importance of following the procedure completely, but also must be able to detect interferences and compensate for them. The analysis procedure for using the Quantab titrator strip is a little more complicated than the procedure for the specific ion probe, but it requires little technical expertise.

Considering each of the criteria, which are summarized in Table 1, for selecting the method for determining the chloride content of concrete, the specific ion probe was determined to be most suitable for the purpose intended. First, the apparatus required for the spectrophotometer and the digital titrator is more suited for use in the laboratory than in the field. Second, both of those procedures require a certain level of expertise to achieve meaningful results. Finally, the Quantab titrator strips do not provide the accuracy that is desirable for determining the time to depassivation and, at times, may require an excessive amount of time for analysis.

EFFECTS OF CEMENT CONTENT

A comparison of the results for the effects of cement content on the specific ion electrode method encompassed using the

accuracy test results ($w/c = 0.47$) along with the results of the testing of 0.50 and 0.40 w/c slab series. As shown in Figure 5, it appears that there is no significant effect of cement content on the performance of the specific ion probe. In addition, a statistical analysis of the results indicated there was no correlation between the results obtained for chloride content using the specific ion probe and cement content.

EFFECTS OF REACTION TEMPERATURE

The results obtained for the specific ion probe during this series of tests were compared with the results obtained for the specimen from the first series of tests to determine the effects of temperature.

Figure 6 shows the relationship between the correction factor for the specific ion probe suggested by the results of the regression analysis relative to the reaction temperature.

SUMMARY AND CONCLUSIONS

The objective of this study was to identify a field procedure for determining the chloride content of concrete. This objective was accomplished by a preliminary investigation of four select methods to determine their effectiveness in measuring the chloride content of concrete followed by a subsequent analysis of the select method to determine the effects of cement content and reaction temperature. Ultimately, a field procedure for determining the chloride content in concrete will be validated.

Results from the initial phase of the investigation indicated that the Quantab titrator strips would provide a rough estimate of the chloride content in a concrete specimen.

The results of the tests using the spectrophotometer indicated that reasonable estimates of chloride content could be obtained particularly for low levels of chloride.

The digital titrator may also be used to obtain good estimates of chloride content in concrete specimens. This procedure allows for accuracy in measuring the chloride content

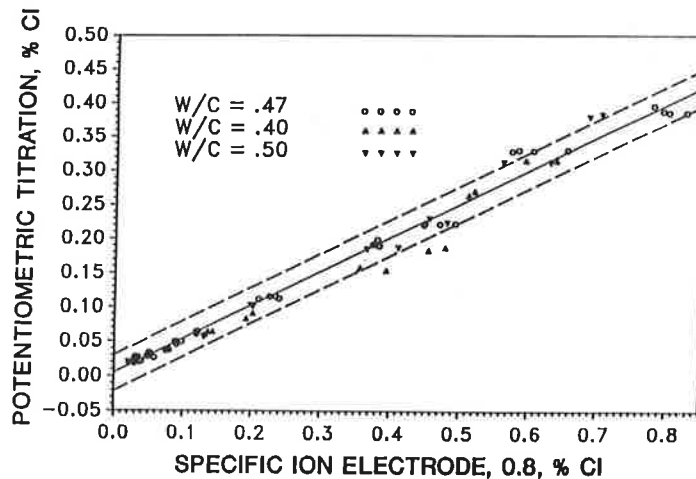


FIGURE 5 Potentiometric titration versus specific ion probe for different cement contents.

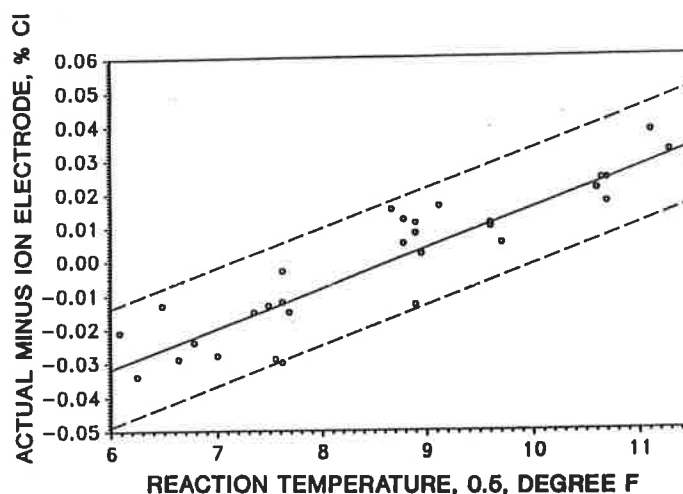


FIGURE 6 Temperature correction for specific ion probe.

over a broader range of contamination levels than with the spectrophotometer.

The specific ion probe provided more accuracy in measuring chlorides in concrete than the previous methods tested. In addition, less than 5 min per specimen was required for the analysis procedure during the laboratory investigation.

The second and third phases of the investigation indicated the specific ion probe test results were not affected by different cement contents but were affected by changes in chloride extraction temperature. Consequently, a correction factor for temperature was developed.

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