

Chloride Content of Portland Cement Concrete Powder by a Method Using Flocculation

K. RAMAMURTI AND G. P. JAYAPRAKASH

A simple and rapid method of determining chloride in portland cement concrete powder is described. This method can be used under field conditions in a portable laboratory. An organic flocculant is used to flocculate the insoluble portion from a portland cement concrete powder suspension in hot water. The clear decant is analyzed for chloride content using a chloride ion-selective electrode.

The minimum quantity of chloride required to initiate the corrosion of steel in concrete is called the chloride content corrosion threshold. Although this concept has been well received, an agreed-upon corrosion threshold has not found wide acceptance. Lewis (1) reported that the water-soluble chloride threshold is 0.15 percent by weight of cement. The American Concrete Institute (ACI) Committee 222 Report 222 R-85(89) (2) cites the work of Lewis (1). It also cites later studies by FHWA (3), California (4), and New York (5) that also demonstrate that a water-soluble chloride content as low as 0.15 percent (or 0.20 percent acid-soluble chloride) is sufficient to initiate corrosion of embedded steel in concrete exposed to chlorides in service. Hence, ACI Committee 222 recommended that the acid-soluble chloride content limit not exceed 0.20 percent (2).

Many bridge design engineers, however, are more interested in the more readily available water-soluble chlorides of in-service concrete structures, that is, the chloride fraction that is most likely to be involved in current or near-future corrosion of bridge-reinforcing steel. Hence, the determination of chloride content of concrete structures is important in relation to corrosion potential, and a simple procedure that could be used in field studies is of much value.

BACKGROUND

In concrete, chloride is present both in water-soluble and insoluble forms. During the last 20 years, methods have been developed to determine the chloride content of concrete. Berman (6) developed a wet-chemical method for determination of the total chloride content of concrete. This method involves the boiling of powdered concrete with acidified water, vacuum

filtration, and titration with silver nitrate using a solid state chloride ion-specific electrode.

For the field determination of chloride in portland cement concrete (PCC), Rhodes et al. (7) developed a neutron gamma ray method capable of providing a rapid and nondestructive survey of total chloride content of concrete bridge deck at the depth of the uppermost mat of reinforcing steel. However, the inordinate high cost of the equipment, together with the periodic maintenance costs and the need for skilled scientific personnel for operating the assembly, limits the use of this procedure.

For the corrosion of steel in concrete, it is the water-soluble segment that is most important. Therefore, modifying Berman's wet-chemical method (6), Morrison et al. (8) have reported a method to determine the water soluble chloride content of PCC. Their method, hereinafter referred to as the water-soluble chloride method, extracts the water-soluble chloride in powdered concrete with boiling water. This step is followed by vacuum filtration, acidification of the filtrate, and final titration with silver nitrate solution using a chloride ion-specific electrode. The values obtained by the water-soluble chloride method are lower than those obtained by the Berman method. The FHWA laboratories report water-soluble chloride content in concrete powder samples as 75 to 80 percent of the total chloride in concrete (9). This fraction agrees with the findings of Morrison et al. (8).

Another available method is the rapid in situ determination of water-soluble chloride ion in PCC developed in Kansas by Morrison et al. (8). This method involves drilling a 19-mm-diameter clean hole to the desired depth downward from concrete surface, using a vacuum drilling method developed in Kansas (10).

The Kansas vacuum drilling technique consists of a vacuum drill system that allows the preparation of a uniform size and depth hole that is free of pulverized concrete. A vacuum swivel chuck that is fitted into a standard Jacobs chuck is used. A vacuum hose from a shop vacuum is attached to the swivel outlet and removes the powder produced by drilling. The drill is used with a hollow 19-mm-diameter carbide-tipped bit, and a drill stop that can be adjusted on the bit shank to provide a uniform predetermined hole depth. The drill stop is designated to contact the bridge surface away from the hole to minimize the chance of high-chloride surface chips falling into the drilled hole. An in-line filter for the drill vacuum system is constructed. This collector fits between the drill chuck vacuum connection and the hose from vacuum cleaner. Glass fiber filter paper (Whatman, GF/A) of 11-cm diameter,

K. Ramamurti, Bureau of Materials and Research, Kansas Department of Transportation, Topeka, Kans. 66611. Current address: 678 Tiffany Court, Sunnyvale, Calif. 94087. G. P. Jayaprakash, Bureau of Materials and Research, Kansas Department of Transportation, Topeka, Kans. 66611. Current affiliation: Transportation Research Board, 2001 Wisconsin Avenue, N.W., Washington, D.C., 20007.

chloride-free, high-volume, which retains particles greater than 1 μm in diameter, retains essentially 100 percent of the sample that is removed from the hole. The powder and the filter paper are then transferred to a sample bottle and returned to the laboratory for chloride analysis.

In the clean hole, a measured amount of borax buffer (pH 9) is introduced. A chloride ion-sensitive electrode attached to a stirring mechanism is directly inserted and stirred. After 90 sec, the potential across the electrode is measured and the values are converted to chloride values using a calibration curve. The average estimation time per sample is 5 min, which includes the time involved in moving the equipment to a new sample site. Although the rapid *in situ* method is used in locations where a hole can be drilled vertically down from a concrete bridge deck, it cannot be used in situations where vertical holes cannot be drilled downward (i.e., in structural members such as piers, abutments, and parapet walls). Hence, for many situations concrete samples for chloride analysis must be obtained by suitable procedure. In the late 1980s, further simplification of the Kansas water-soluble chloride method was explored by the Kansas Department of Transportation (KDOT) by using organic flocculants. A simple method for chloride analysis of such samples is described in this report.

The use of flocculants to sediment phosphate suspensions has been reported by LaMer et al. (11). Magnifloc 834A, an organic flocculant, has been successfully used in the determination of nitrite in powder samples of PCC (12). The flocculant method should improve the quality of the decanted liquid for chloride testing. Magnifloc 834A is a white powder, having anionic characteristics and a specific gravity of 628 to 720 kg/m^3 with a relative molecular mass between 8 to 10 million. Magnifloc 834A, while sedimenting PCC powder slime, also caused the formation of firm flocs by decantation.

EXPERIMENTAL

In order to determine the effect of the presence of Magnifloc 834A on the results of chloride content determinations, experiments were conducted with standard sodium chloride solutions of different concentrations. The results indicated that inclusion of several levels of the flocculant had no effect on the determined chloride values. The next step was directed towards using the flocculant (Magnifloc 834A) in determining the chloride content in sodium chloride-doped concrete.

Several sodium chloride-doped concrete beams were prepared with a chloride content that ranged from 0.35 to 1.42 kg/m^3 . Dry-powder samples of concrete was obtained from these beams using the Kansas vacuum drilling technique (10). A total of 252 samples, representing seven locations on each beam and three levels at each location, was obtained from 12 beams. Each of the 252 samples was split to provide two sets of samples. The chloride content of one set of samples was determined according to the water-soluble method. The second set of samples was used to evaluate the flocculant method.

In the flocculant method, 5 g of the powdered PCC sample weighed to the nearest milligram were quantitatively transferred to a 125-ml Erlenmeyer flask. After the addition of 75 ml of boiling water to the powdered material, the flask was

continuously swirled to obtain a uniform suspension. To this suspension, 1 ml of flocculant (Magnifloc 834A, 100 ppm) was added, swirled for 15 sec, and allowed to stand for 2 min. Soon after, the clear supernatant was decanted into a clean 250-ml beaker. The extraction was repeated with 0.5 ml of flocculant. Then the clear supernatant was decanted and combined with the first extract in the 250-ml beaker. During the initial trials, the third extraction proved to be of no benefit. Hence only two extractions of each sample were made in this study. The combined extracts were acidified with 2 ml of nitric acid and chloride content was determined using a chloride ion-sensitive electrode as in Gran end point determination procedure. The results of the flocculant method are presented in Table 1 along with those of the water-soluble method. Although the chloride values presented in Table 1 are an average of 21 determinations, calculation of the standard deviation was not considered, because the 21 chloride values obtained for each beam by each method were identical.

Data presented in Table 1 indicate that there is no significant difference between the values obtained by the water-soluble chloride and flocculant methods. The chloride contents determined by the flocculant method were 99.6 to 100 percent of those obtained with the water-soluble chloride method. The foregoing results indicated that the accuracy of the flocculant method was equal to that of the water-soluble chloride method. Because of thorough mixing, the distribution of salt in laboratory samples was relatively homogeneous.

FIELD SAMPLES

Chloride distribution in field concrete is nonhomogeneous. Therefore, other salt-contaminated samples were analyzed by both methods. Initially, samples from two concrete slabs that were exposed to outdoor salting during the work related to another KDOT project (13) were used. Each sample was split into two and the duplicates were analyzed by both methods. The range of water-soluble chloride contents in these samples was from 0.24 to 4.77 kg/m^3 . Values of chloride content ob-

TABLE 1 CHLORIDE DETERMINATIONS OF NaCl-DOPED CONCRETE BEAMS

Beam No.	Cl^- Expressed as kg/m^3		
	Actual Addition	Water-Soluble Method ^a	Flocculant Method ^{a,b}
613	0.350	0.404	0.404
614	0.350	0.402	0.402
615	0.350	0.404	0.402
621	0.710	0.727	0.726
623	0.710	0.727	0.727
625	0.710	0.727	0.725
631	1.062	1.051	1.047
634	1.062	1.051	1.047
635	1.062	1.051	1.047
640	1.416	1.374	1.368
643	1.416	1.374	1.368
645	1.416	1.374	1.368

NOTE: The data for each method represent 252 chloride determinations, and a total of 504 determinations for the two methods.

^aChloride contents indicated represent average of 21 samples from each beam. Little or no variation was found in the values of the 21 samples.

^bData are for duplicate samples.

tained by the flocculant method were 73 to 100 percent of those obtained by the water-soluble chloride method. A plot of Cl⁻ contents determined using water-soluble chloride method, against those of the flocculant method is shown in Figure 1. Linear regression analysis of the data indicates a correlation coefficient of 0.997. Again, this value indicates that the accuracy of the flocculant method is equal to that of the water-soluble chloride method.

The two factors that are of most concern that might have been responsible for the observed differences in the determined chloride values are differences in the two analytical methods and differences in the sample locations. In order to investigate the effect on the results caused by differences in methods, the data shown in Figure 1 were reexamined. The percent of sample pairs out of the total number of pairs analysed by both the water-soluble and the flocculant methods was determined. The findings are presented in Table 2. Almost 28 percent of the sample pairs did not have any difference and none of the sample pairs had a difference in chloride value of more than 0.59 kg/m³. The range of chloride content in these samples was from 0.24 to 4.77 kg/m³.

In order to determine the variation of chloride content caused by sample location, 27 cores of 2-in. (50.8-mm) diameter from concrete bridge decks, subjected to winter salting, were used. Each core was longitudinally split into two halves and each half was sliced into 3/4-in. (19-mm) layers

TABLE 2 VARIATIONS IN CHLORIDE CONTENT OF CONCRETE—ANALYTICAL METHOD

Differences in Cl ⁻ Content, kg/m ³	Observed Differences in Cl ⁻ due to Analytical Method ^a	
	Samples (%)	Cumulative (%)
>0.59	0	0
0.44-0.59	14	14
0.29-0.44	18.6	32.6
0.15-0.29	25.6	58.2
0-0.15	14	72.2
0	27.8	100

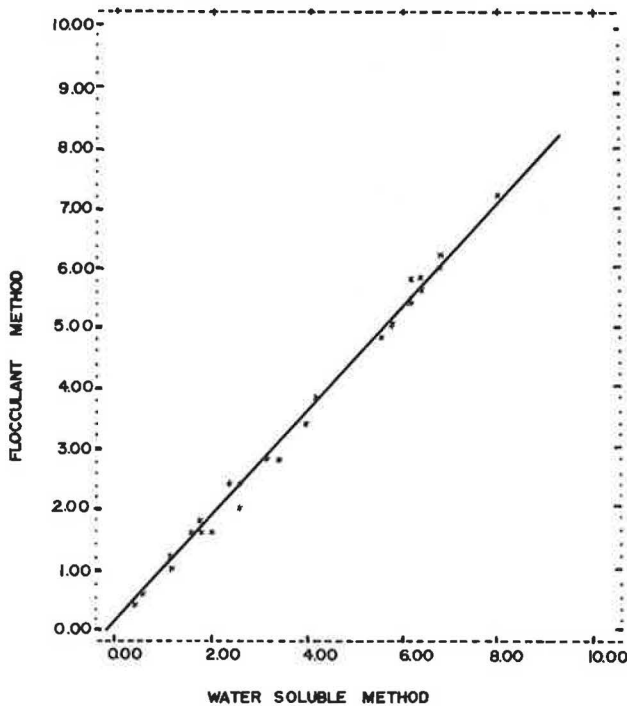
^aDuplicate samples of salt-contaminated outdoor exposure slabs analyzed using the water soluble and flocculant methods. Range of the salt content was 0.24 to 4.76 kg/m³ (Cl⁻).

(Figure 2). Chloride content of each of the layers of the two core halves was determined using only the water-soluble chloride method. The results are presented in Table 3. The data indicate that 26 percent of the sample pairs had no difference in their chloride content and almost 15 percent of the sample pairs had a difference in chloride content of 0.59 kg/m³. The range of chloride content in these samples was from 0.04 to 4.31 kg/m³, which was comparable to that of samples used for comparing the variation in results caused by differences in the two analytical methods.

The investigation of field samples indicated that the variations in salt content of adjacent samples caused by location was greater than that caused by differences in the two methods. The nonhomogeneity of concrete indicated that the salt data obtained using relatively simple methods were equal in significance to those of more sophisticated analyses.

SUMMARY AND CONCLUSION

Knowledge of chloride content, particularly the water-soluble fraction, of reinforced-concrete structures is believed to be important in regard to corrosion of steel and hence the durability of the structures. A new method that uses an organic flocculant in the determination of chloride content of powdered concrete was developed. Laboratory and field samples



VARIABLE X: WATER SOLUBLE
 MEAN OF X = 2.79616
 S.D. OF X = 2.09307
 MAXIMUM X = 8.08
 MINIMUM X = .41
 VARIABLE Y: FLOCCULANT
 MEAN OF Y = 2.50825
 S.D. OF Y = 1.8519
 MAXIMUM Y = 7.27
 MINIMUM Y = .41
 NUMBER OF PAIRS (N) = 44
 CORRELATION COEFFICIENT (R) = .997
 DEGREE OF FREEDOM (DF) = 42
 SLOPE (M) OF REGRESSION LINE = .881711
 Y INTERCEPT (B) FOR THE LINE = .0428471

FIGURE 1 Plot of Cl⁻ values by water-soluble chloride method versus flocculant method (1 unit = 0.59 kg/m³).

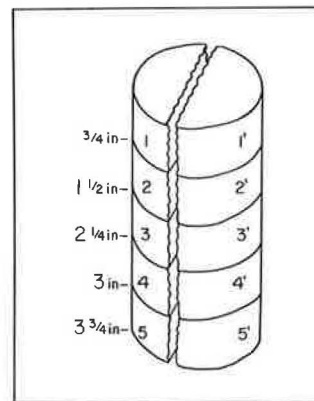


FIGURE 2 Two halves of a 2-in.-diameter bridge deck concrete core, each split into 3/4-in. layer, that provided adjacent salt samples for Cl⁻ analysis.

TABLE 3 VARIATIONS IN CHLORIDE CONTENT OF CONCRETE—SAMPLE LOCATIONS

Differences in Cl ⁻ Content, kg/m ³	Observed Differences in Cl ⁻ due to Sample Locations ^a	
	Samples (%)	Cumulative (%)
>0.59	14.8	14.8
0.44–0.59	3.7	18.5
0.29–0.44	3.7	22.2
0.15–0.29	18.5	40.7
0–0.15	33.3	74.0
0	26	100

^aTwo adjacent core halves of bridge deck salt samples (see Figure 2) analyzed using the water soluble method only. Range of the salt content was Cl⁻ = 0.04 to 4.31 kg/m³.

were analysed by the water-soluble and the flocculant methods. The variation in chloride content of juxtaposing concrete samples was greater than that caused by differences in these two methods. It is concluded that the flocculant method has the same level of accuracy and provides results as rapidly as the water-soluble chloride method. Therefore, the flocculant method is presented as an alternative method for the existing methods to determine the water-soluble chloride content of powdered concrete samples.

ACKNOWLEDGMENT

The authors thank Carl F. Crumpton, Kansas Department of Transportation, for his encouragement and support for this work.

REFERENCES

- D. A. Lewis. Some Aspects of the Corrosion of Steel in Concrete. *Proc. 1st International Congress on Metallic Corrosion*, London, 1962, pp. 547–555.
- Corrosion of Metals in Concrete. ACI 222R–85(89). ACI Committee 222 Report, American Concrete Institute, Detroit, Mich., 1985, 1989.
- K. C. Clear. *Time-to Corrosion of Reinforcing Steel in Concrete Slabs. Vol. 3. Performance After 830 Daily Salt Applications*. Report FHWA-RD-76-70. FHWA, 1976.
- R. F. Stratful, W. J. Jurkowitch, and D. L. Spellman. Corrosion Testing of Bridge Decks. In *Transportation Research Record 539*, TRB, National Research Council, Washington, D.C., pp. 50–59.
- W. P. Chamberlain, R. J. Irwin, and D. E. Ansler. *Waterproofing Membranes for Bridge Deck Application*. Research Report 52 (FHWA-NY-77-59-1). New York State Department of Transportation, Albany, 43 pp.
- H. A. Berman. *Determination of Chloride in Hardened Portland Cement Paste, Mortar, and Concrete*. Report FHWA-RD-72-12, FHWA, U.S. Department of Transportation, 1972.
- J. R. Rhodes, J. A. Stout, R. D. Sieberg, and J. S. Schindler. *In Situ Determination of the Chloride Content of Portland Cement Concrete Bridge Decks*. Report FHWA/RD-80/030. Final Report, FHWA, U.S. Department of Transportation, 1980.
- G. L. Morrison, P. V. Yash, K. Ramamurti, and W. J. Gilliland. *Rapid In Situ Determination of Chloride Ion in Portland Cement Concrete Bridge Decks*. Final Report, Report FHWA-KS-RD-75-2. Kansas Department of Transportation, Topeka, 1976.
- NCHRP Synthesis Report 57: Durability of Concrete Bridge Decks*. TRB, National Research Council, Washington, D.C., 1979.
- F. W. Stratton and B. F. McCollum. *Repair of Hollow or Softened Areas in Bridge Decks by Rebonding with Injected Epoxy Resin or Other Polymers*. Report K-F-72-5. Kansas Department of Transportation, Topeka, 1974.
- V. K. LaMer, R. H. Smellie, Jr., P. K. Lee, and K. Ramamurti. *The Preparation and Evaluation of Superior Flocculating Agents for Phosphate Slimes*. Progress Report NYO-7403. United States Atomic Energy Commission, Columbia University, New York, 1956.
- K. Ramamurti. Method for Determination of Water Soluble Nitrite in Concrete. Appendix C in *Electro-Osmotic Techniques for Removal of Chloride from Concrete and for Emplacement of Concrete Sealants*. Kansas Department of Transportation, Topeka, 1982.
- G. P. Jayaprakash, J. E. Bukovatz, K. Ramamurti, and W. J. Gilliland. *Electro-Osmotic Techniques for Removal of Chloride from Concrete and for Emplacement of Concrete Sealants*. Final Report, Report FHWA-KS-82-2, Kansas Department of Transportation, Topeka, 1982.

Publication of this paper sponsored by Committee on Basic Research Pertaining to Portland Cement and Concrete.