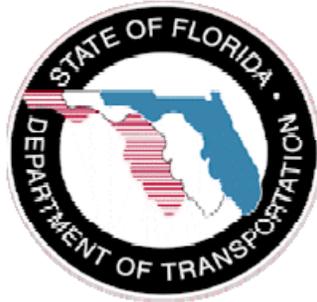


State of Florida  
**Department of Transportation**



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Results of an Interlaboratory Study to  
Evaluate the Florida method of Test for  
Determining Low Levels of Chloride in  
Concrete and Raw Materials (FM5-516)

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## Introduction

Due to the deleterious effect of chloride in concrete, it is important to be able to accurately determine the chloride content present in both freshly batched concrete as well as concrete that has been exposed to saline environments. This can be a challenge due to the lack of homogeneity between and within concrete mixes and interactions of mix ingredients with reagents that are commonly used in test methods (Poor, 2011). An interlaboratory study was conducted in order to investigate proposed revisions to the Florida Method of Test for Determining Low Levels of Chloride in Concrete and Raw Materials (FM 5-516). All of the revisions seek to reduce ambiguity to the method, add quality assurance/quality control steps, or address the issue with low pH measurements (Poor, 2010). In order to determine the precision of the revised method, a round robin study of six laboratories was carried out.

## Inspection of Data

Although every effort is made to avoid mistakes, errors can still occur. Initial assessment of the data yielded the following concerns:

- The possibility of more than one operator per laboratory performing the testing.
- Differences in the number of aliquots used to bring the sample to scaling potential. It is not clear whether this was an issue of segregation and insufficient stirring, losing count of the number of aliquots used, or some other cause.
- Failure to exceed the scaling potential.
- Ambiguity of the mass of powder that was tested. The test method requires the mass to be recorded to one-thousandth of a gram (1 mg). In some instances, it is unclear whether the powder was weighed correctly and the recording was truncated, or if the sample was incorrectly measured to the nearest gram.
- Some samples were out of range, meaning that the difference between replicate readings was greater than allowed by the test method. These instances should have been disregarded and retested per the test method.
- Failure to adhere to the testing schedule.
- Discrepancies in value between the official report and the round robin spreadsheet.
- Using the incorrect volume of silver nitrate ( $\text{AgNO}_3$ ) to determine the scaling potential.

Unfortunately, due to unexpected circumstances during the testing period, the opportunity to clarify some of these issues was lost. The issues occurred in various frequencies and combinations among each laboratory which is detailed below.

- **Laboratory 1** – This laboratory deviated from the test method in only a few instances. The main concern was that two different technicians ran the samples. While this was never specifically addressed in the participant instructions, it obviously is preferable to have a single operator. This situation was completely beyond their control and they did finish testing even if it was not an ideal situation. The first technician performed all of the

testing for the first five weeks, and a second technician conducted the testing for week six. One gray area in the test method that became apparent during the round robin involves the number of aliquots used to bring the replicates up to the scaling potential. Assuming the concrete powder is well mixed, the number of aliquots should be the same for all three replicates. This was a recurring problem for this laboratory. It is not clear if this was an issue of segregation and insufficient stirring. Another problem arose in the final week of testing; the technician failed to pass the scaling potential voltage for replicate A and a different number of aliquots of silver nitrate were used for the other two replicates. If the scaling potential had been passed, the number of aliquots would have matched. The last area concerning compliance with the test method involved the mass of the powder that was tested. The test method requires the mass to be recorded to an accuracy of 1 mg. It is unclear if the powder was weighed to that accuracy and the number was truncated or if the replicates were weighed to the nearest gram.

- **Laboratory 2** - Overall, this laboratory had only a few issues identified in the round robin. The main problem that this technician had was in meeting the scaling potential. In addition to not passing the scaling potentials, occasionally the technician used different aliquots of  $\text{AgNO}_3$ . If matching aliquots of  $\text{AgNO}_3$  had been used, the scaling potential for those replicates would have been met or exceeded. While this is not specifically addressed in FM 5-516 or in the participant instructions, if the concrete is well mixed, the number of aliquots should usually be the same for all three replicates. Again, it is not clear if this was an issue of segregation and insufficient stirring. The next issue is that the technician's name or identification number is not on the test report, making it impossible to know how many technicians performed the test. This was not specifically addressed in the participant instructions, but it is obviously preferable to have a single operator. The last area concerning compliance with the test method involved the mass of the powder that was tested. The test method requires the mass to be recorded to an accuracy of 1 mg. It is unclear if the powder was weighed to that accuracy and the number was truncated or if the replicates were weighed to the nearest gram.
- **Laboratory 3** – This laboratory had several issues affecting the consistency of the round robin. The most critical concern involved one sample which was out of range. In addition to that sample being out of range, replicate B failed to meet the scaling potential. Even though only one sample was out of range, this was out of compliance with the test method and according to the FM 5-516, the sample should have been retested. Another area of concern is that 47% of the time the technician did not reach the scaling potential. While it is unclear at this point how that affected the round robin, this is not in compliance with the test method. Another issue which arose was due to problems with their equipment; this resulted in failure to meet the schedule set forth in the participant instructions. However, they quickly caught up and provided the results in a timely manner. Finally, the last area concerning compliance with the test method involved the mass of the powder that was tested. The test method requires the mass to be recorded to an accuracy of 1 mg. It is unclear if the powder was weighed to that accuracy and the number was truncated or if the replicates were weighed to the nearest gram.

- **Laboratory 4** – This laboratory had numerous deviations from the test method. The first issue involved discrepancies between the official report and the spreadsheet showing the final results. There were four samples in the official report which were one tenth the value that was reported in the round robin spreadsheet. It is unclear why the final results were multiplied by 10. There was no explanation given for this manipulation which causes questioning of the samples' validity. Another critical concern affecting the quality of the round robin results involves 7% of the samples being out of range. All samples that were outside of the acceptable range should have been retested. Failure to do so results in the laboratory being out of compliance with the test method. Another area of concern is that 35% of the time the technician did not reach the scaling potential. In fact, two samples failed to meet scaling potentials by more than 120 mV. While it is unclear at this point how that affected the round robin results, this is not in compliance with the test method. Yet another problem involved the number of aliquots needed to pass the scaling potentials. The technician frequently used different aliquots. It seems unlikely that this amount of variation is the result of normal inconsistencies. Many circumstances could be responsible for this situation including (but not limited to): segregation as a result of inadequate stirring, inaccuracy in weighing the sample, or human error (losing count of the number of initial aliquots to reach scaling potential). Another concern involved the number of technicians that tested the samples. One technician recorded his name on the form most of the time; however, some forms have no name listed for the technician. This could have been an oversight or multiple technicians could have performed the tests. This was not specifically addressed in the participant instructions, but it is obviously preferable to have a single operator. An additional issue involved the laboratory failing to meet the schedule set forth in the participant instructions. Since the purpose of the schedule was to test within a tight time frame with the expectation that equipment conditions are unlikely to change significantly in that period of time, this extended delay created uncertainty regarding the validity of the test. Finally, the last area concerning compliance with the test method involved the mass of the powder that was tested. The test method requires the mass to be recorded to an accuracy of 1 mg. It is unclear if the powder was weighed to that accuracy and the number was truncated or if the replicates were weighed to the nearest gram.
- **Laboratory 5** – This laboratory had several issues in their procedure during the round robin. One concern involved the 0.1 N silver nitrate used to determine the scaling potential. The test method specifies that to obtain the scaling potential, 1 ml of  $\text{AgNO}_3$  is added to 100 ml of deionized water; however, this laboratory determined the scaling potential based on adding only 0.5 ml. This is not in compliance with the test method. Another area of concern, 68% of the time the technician did not reach the scaling potential. While it is unclear at this point how that affected the round robin, this is not in compliance with the test method. Another concern involved the number of technicians that tested the samples. It is not clear if there were one or two technicians due to the manner in which it was recorded.

- **Laboratory 6** - The only area where this technician was not compliant with the test method involved either weighing the powder or in recording the weight. The test method requires the mass to be recorded to an accuracy of 1 mg. It is unclear if the powder was weighed to that accuracy and the number was truncated or if the replicates were weighed to the nearest gram.

**Table 1.** A summary of the results for the laboratories that participated in the Round Robin.

Laboratory	Failed to meet scaling potential	Incorrect volume used for blank*	Out of Range	More than 1 Technician	Stayed on schedule?
1	1%	0%	0%	Yes	Yes
2	10%	0%	0%	?	Yes
3	47%	0%	1%	No	No
4	35%	0%	7%	?	No
5	68%	14.4%	0%	?	Yes
6	0%	0%	0%	No	Yes

\*For the 0.1 Silver Nitrate the scaling potential was determined using 0.5 ml instead of 1.0 ml.

### Analysis of Data

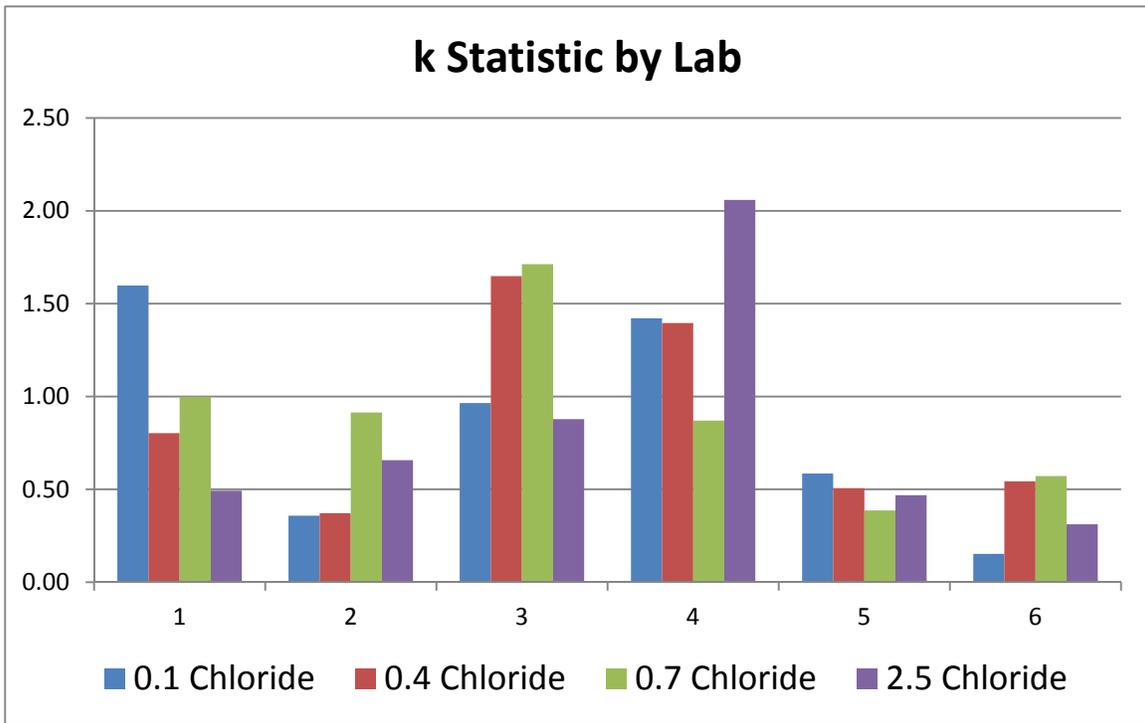
The results are averages of three replicates which were tested at six different laboratories. Testing was scheduled to occur every other week for twelve weeks. Table 2 shows the test results from the six laboratories that participated in the round robin study.

Using the method suggested in ASTM E178 (2008), none of the individual test determinations exceeded the critical value of 0.988 and therefore no extreme individual values were eliminated.

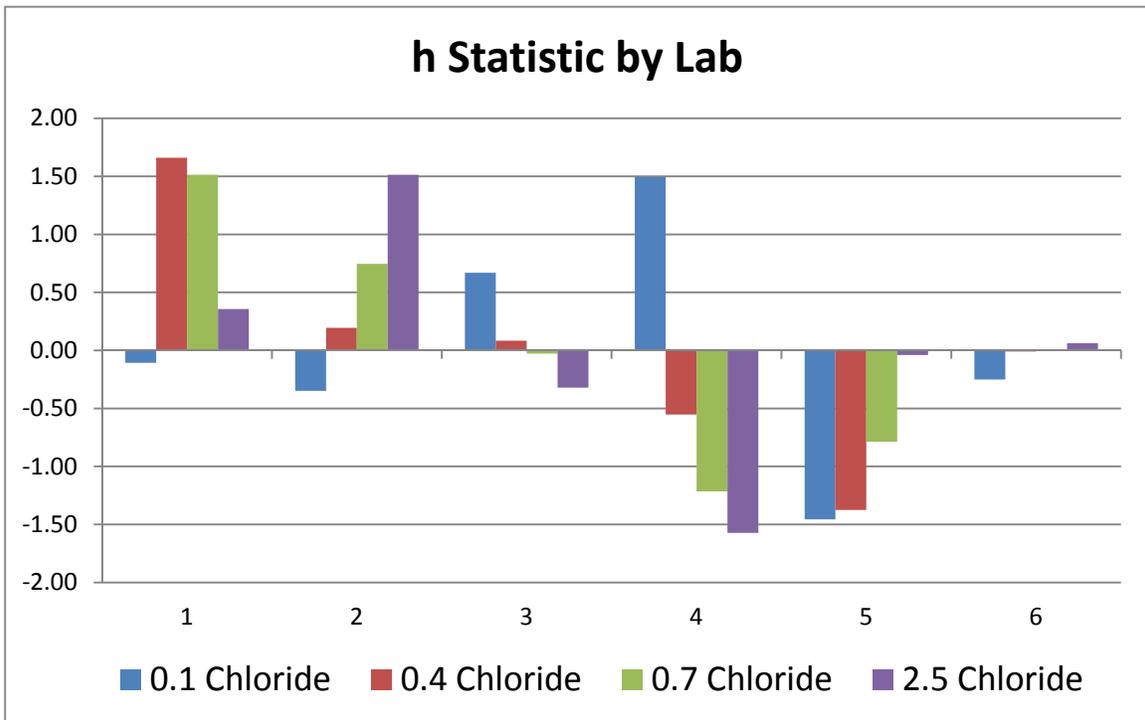
The plots of between-laboratory and within-laboratory variances for each material are the first indication of inconsistencies amongst the data (ASTM C802, 2009). Figure 1 shows the  $k$  statistic of each laboratory, which represents the within-laboratory consistency. Investigation of Laboratories 1, 3, and 4 is warranted based on their  $k$  statistics exceeding 1. The  $h$  statistics are shown in Figure 2, which represent the between-laboratory consistency. Laboratories 1, 4, and 5 have the largest average absolute value  $h$  statistics of 0.9096, 1.208, and 0.9148, respectively (ASTM E691, 2012). The plotted average of each concrete mix against each laboratory in Figure 3 shows the same pattern for each laboratory; therefore, there is no evidence of interactions between the laboratories and chloride content (ASTM C802, 2009).

**Table 2.** Chloride content values as reported by each laboratory.

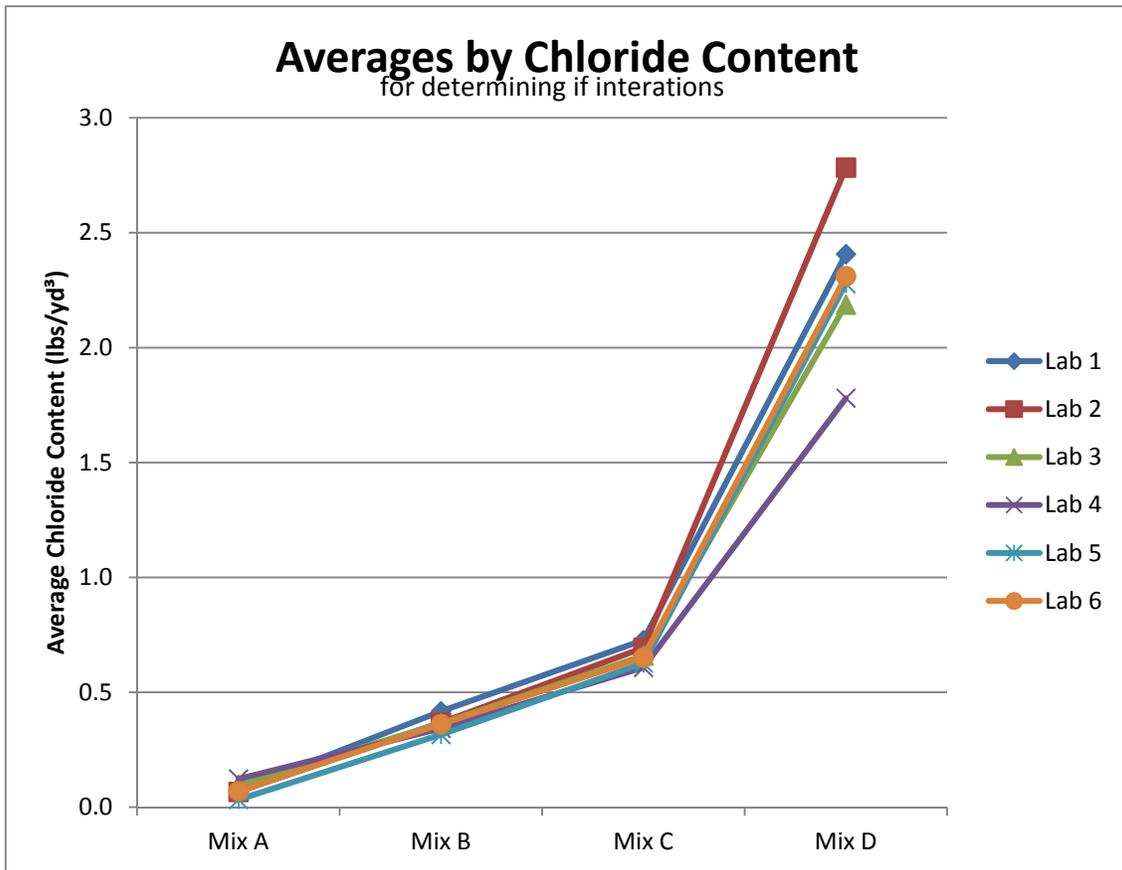
Laboratory	Test Week	Test Results			
		Mix A	Mix B	Mix C	Mix D
1	1	0.122	0.432	0.737	2.386
	2	0.077	0.419	0.793	2.655
	3	0.019	0.371	0.689	2.321
	4	0.093	0.426	0.712	2.393
	5	0.102	0.434	0.741	2.503
	6	0.032	0.422	0.689	2.184
2	1	0.081	0.383	0.713	3.137
	2	0.064	0.372	0.663	2.702
	3	0.066	0.358	0.665	2.601
	4	0.072	0.368	0.655	2.591
	5	0.063	0.354	0.729	2.939
	6	0.054	0.374	0.734	2.729
3	1	0.113	0.360	0.671	2.621
	2	0.127	0.446	0.789	2.366
	3	0.108	0.368	0.635	2.109
	4	0.104	0.355	0.627	1.808
	5	0.068	0.296	0.598	1.991
	6	0.067	0.362	0.638	2.227
4	1	0.137	0.382	0.620	2.897
	2	0.139	0.341	0.599	1.613
	3	0.104	0.325	0.607	2.153
	4	0.058	0.276	0.546	1.723
	5	0.142	0.350	0.632	1.278
	6	0.157	0.386	0.643	1.016
5	1	0.044	0.333	0.621	2.177
	2	0.025	0.295	0.631	2.081
	3	0.012	0.317	0.642	2.318
	4	0.030	0.304	0.599	2.288
	5	0.032	0.331	0.631	2.535
	6	0.054	0.314	0.636	2.270
6	1	0.065	0.379	0.679	2.390
	2	0.075	0.347	0.638	2.334
	3	0.066	0.372	0.666	2.412
	4	0.070	0.342	0.614	2.153
	5	0.072	0.353	0.652	2.355
	6	0.071	0.375	0.655	2.222



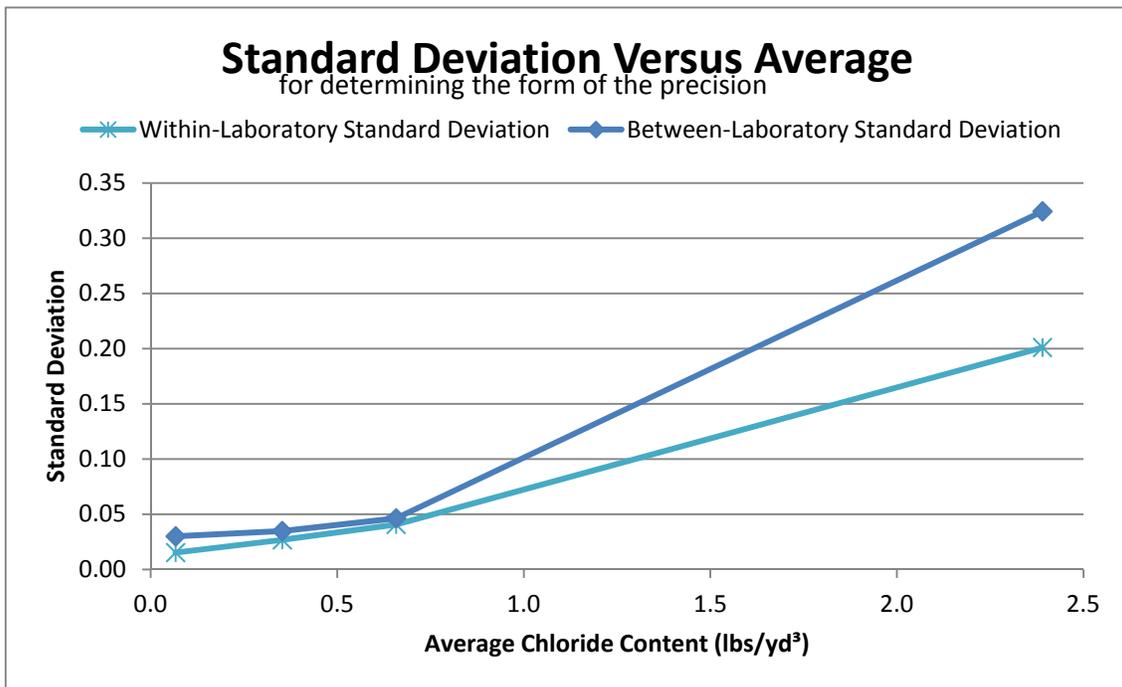
**Figure 1.** The within-laboratory consistencies for each laboratory.



**Figure 2.** The between-laboratory consistencies for each laboratory.



**Figure 3.** The computed averages of each mix among the laboratories.



**Figure 4.** The between- and within-laboratory standard deviations for each chloride content.

Based on the reoccurring between-laboratory and within-laboratory inconsistencies of Laboratories 1 and 4, their set of results for the duration of testing are unrepresentative and will not be included in the development of the precision statements. Refer to the Inspection of Data section for potential sources for these inconsistencies.

Figure 4 shows the recalculated within-laboratory and between-laboratory standard deviations for each mix after removal of Laboratories 1 and 4. The graph shows that the standard deviation is relatively constant for chloride contents below 1.0 lbs/yd<sup>3</sup> (ASTM C802, 2009).

### **Precision and Bias Statements**

The following precision statements were prepared in accordance with ASTM C670 (2010).

The single-operator standard deviation of a single test result (where a test result is, as defined in this test method, the average of three separate measurements) has been found to be 0.0255 lbs/yd<sup>3</sup> for chloride content below 1.0 lbs/yd<sup>3</sup>. Therefore, results of two properly conducted tests (each consisting of the average of three individual measurements) are not expected to differ by more than 0.0721 lbs/yd<sup>3</sup> for chloride content below 1.0 lbs/yd<sup>3</sup>.

The multilaboratory standard deviation of a single test result (where a test result is, as defined in this test method, the average of three separate measurements) has been found to be 0.0326 lbs/yd<sup>3</sup> for chloride content below 1.0 lbs/yd<sup>3</sup>. Therefore, results of two properly conducted tests (each consisting of the average of three individual measurements) on the same material in two different laboratories are not expected to differ by more than 0.0922 lbs/yd<sup>3</sup> for chloride content below 1.0 lbs/yd<sup>3</sup>.

The single-operator and multilaboratory standard deviations for chloride content above 1.0 lbs/yd<sup>3</sup> are 0.2009 lbs/yd<sup>3</sup> and 0.3243 lbs/yd<sup>3</sup>, respectively. Therefore, results of two properly conducted tests within the same laboratory are not expected to differ by more than 0.569 lbs/yd<sup>3</sup>, and results from two properly conducted tests in two different laboratories are not expected to differ by more than 0.9178 lbs/yd<sup>3</sup>. These results and Figure 1 both demonstrate that the test method is prone to more variability above the 1.0 lbs/yd<sup>3</sup> chloride content.

When experimental results are compared with known values from accurately compounded specimens, the test method is found to have no bias (Poor, 2011).

### **Conclusions**

The single-operator and multilaboratory standard deviations based on a previous interlaboratory study with only two chloride contents (rather than the three levels of this study) are 0.0331 lbs/yd<sup>3</sup> and 0.0394 lbs/yd<sup>3</sup>, respectively (Poor, 2011). Therefore, the lower standard deviations found in this round robin study indicate that the proposed revisions to FM 5-516 produce more reliable test results. However, the small sample size and errors in data collection of this study limit the merit of these findings.

## **Acknowledgements**

The Florida Department of Transportation Corrosion Research Laboratory would like to thank all of the laboratories that graciously participated in the testing. Round robins such as this are the only way statistically valid changes can be made to the current test method.

## **References**

Poor, N., 2011. A Revised Method of Test for Determining Low Levels of Chloride Content in Concrete and Raw Materials (FM 5-516) and Preparations for an Inter-Laboratory Study. Prepared for Florida Department of Transportation, Tallahassee, Florida.

Poor, N., 2010. A Single-Operator Study of the Florida Method of Test for Determining Low Levels of Chloride in Concrete and Raw Materials (FM 5-516). Prepared for Florida Department of Transportation, Tallahassee, Florida.

ASTM E178, 2008. Standard Practice for Dealing with Outlying Observations, E 178-08. ASTM International, West Conshohocken, Pennsylvania. p. 18.

ASTM C802, 2009. Standard Practice for Conducting an Interlaboratory Test Program to Determine the Precision of Test Methods for Construction Materials, C 802-09a. ASTM International, West Conshohocken, Pennsylvania. pp. 5-17.

ASTM E691, 2012. Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method, E 691-12. ASTM International, West Conshohocken, Pennsylvania. pp. 8-17.

ASTM C670, 2010. Standard Practice for Preparing Precision and Bias Statements for Test Methods for Construction Materials, C 670-10. ASTM International, West Conshohocken, Pennsylvania. pp. 2-5.