Determination of chloride ion concentrations in concrete by means of near-infrared spectrometry

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ABSTRACT

Concentration of chloride ions was determined with a classical chemical titration method in three types of samples: a cracked concrete core and an undamaged concrete core, both taken from a bridge in Iowa, and also from concrete test samples prepared at Rutgers University. Chloride concentration profiles were obtained. The same samples were the subjected to the near infrared spectrometric determinations of chloride content by two manufacturers of spectrometric instruments. Very good correlation between the chemical and spectrometric measurements was obtained [R^2> 0.96], thus opening the possibility of rapid on-site chloride concentration determination in concrete structures.

Keywords: chloride in concrete, near-infrared spectrometry, rapid determination

1. INTRODUCTION

1.1 Background

Penetration of chloride ions into concrete is a well-known problem, because it eventually results in corrosion of rebars, leading to cracks, spalling, delamination and other roadway defects [1]. The problem is particularly acute in bridge decks, which are subject to frequent salt applications during the winter months. Since there are some 600,000 bridges in the USA, the corrosion and the damage to bridge decks also represents a major economic burden to the maintenance of national infrastructure. It is thus very important to understand the nature and the extent of the chloride penetration into concrete structures, in order to establish the proper scheduling and locations for maintenance and repair procedures.

There are well established chemical titration methods for determining chloride concentrations in concrete [AASHTO T 260-97 [2005]]. However, this method is tedious, slow and expensive. Typically, large cores, several inches in diameter are extracted from bridge decks, then sent to specialized chemical laboratories, where these cores are sliced, pulverized and finally subjected to chemical analysis. Both, water soluble and acid soluble chloride concentration profiles are determined. Of particular importance are chloride concentrations at the depth of rebars, which is typically 2 to 4 inches below the surface. If the corrosion threshold is exceeded, the rebar corrosion is possible and quite likely in due time. It is difficult to predict the penetration of chlorides into concrete. While it is easy to calculate the diffusion of various ions in metals and semiconductor materials, because diffusion coefficients are well known, this is not possible in concrete which has simply too many variables specific to the given structure, e.g., type of concrete, % of cement, water to cement ratio, additives, filler size, type and shape, pH values, loading and age of the structure, etc. Thus, the only reliable way of assessing the chloride penetration is the direct measurement.

In this paper, the application of the near-infrared [NIR] spectrometry to the measurements of chloride concentrations in concrete is presented. Potential for the rapid, low cost assessment of the corrosion problems in bridge decks is discussed.

1.2 Samples for the analysis

Three types of samples were subjected first to the chemical and then to the NIR spectrometric analysis to establish the possible correlation between these two analytical methods. Figure 1 shows a cracked 4” core and the heavy corrosion of rebars, as evidenced by the prominent rust stains. This sample, denoted Core 1, was taken from a bridge in Iowa. Core 2, taken from the same bridge, was undamaged and it showed no signs of corrosion. Finally, three concrete cubes with 3” side, prepared at Rutgers were also subjected to the analysis. The Rutgers samples had known amounts of chloride mixed in, ranging from nominally 0, to 0.03 and 0.15 by weight % of concrete, respectively.

The standard procedure at the chemical analysis laboratory is to slice the core into 0.5 “ slices to obtain samples at different distance from the surface. A part of that slice is then pulverized and subjected to the chemical titration. The remaining portion of the powder in this work was then sent for NIR analysis, to check the results of this novel approach against the standard analytical test.

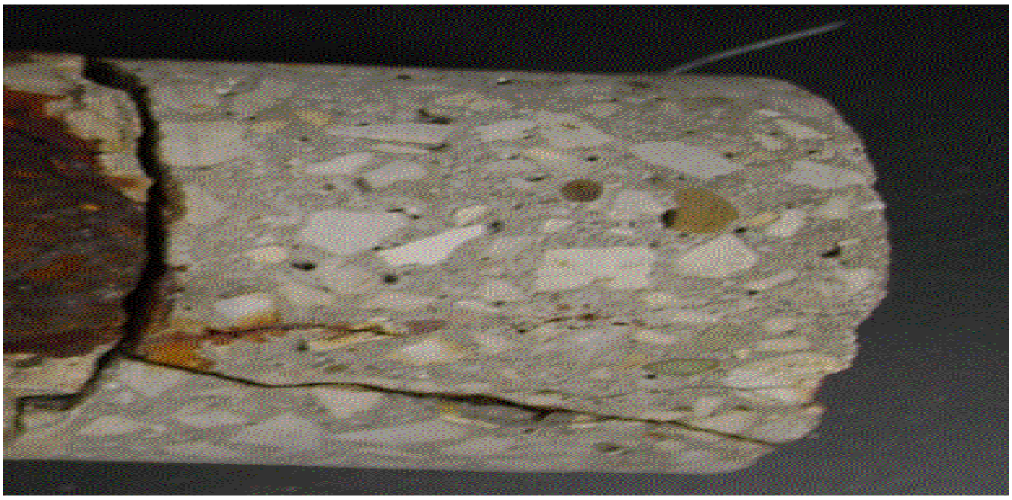

Figure 1. Core 1, taken from an Iowa bridge, 4” diameter. This core shows cracking and a heavy corrosion of the rebar, as evidenced by the heavy rust stain.

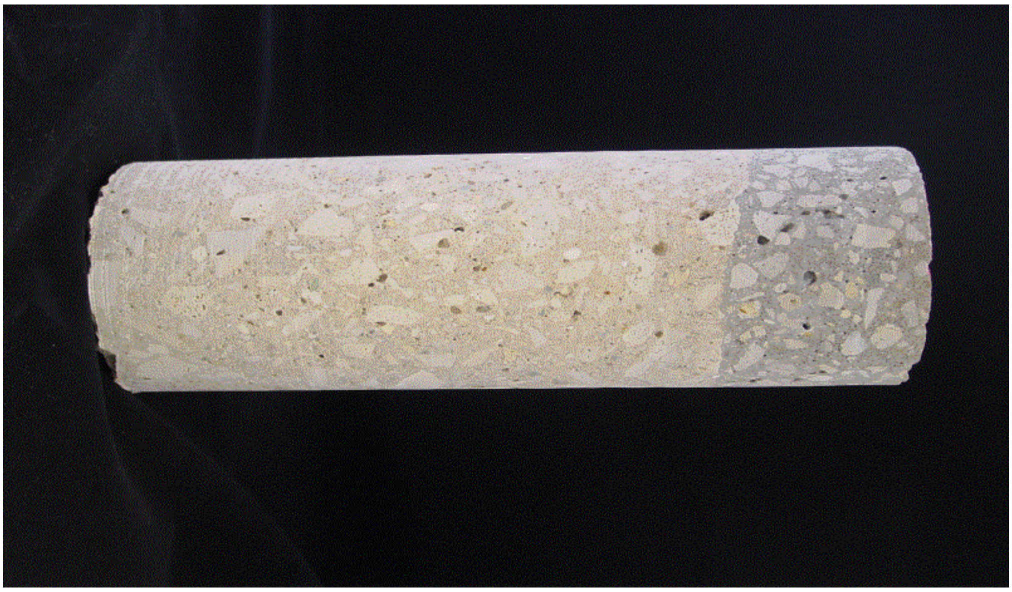

Figure 2. Core 2 taken from the same bridge, also 4” diameter. This core shows no damage. The analysis was done from the surface to the bottom in 1 cm increments.

Figure 3. Concrete cubes with known chloride concentrations, prepared at Rutgers, Cubes are 3” on a side.

2. ANALYTICAL RESULTS

2.1 Chemical analysis results

Chemical analysis was done by the CTL Group, from Skokie, Illinois. Both the water extractable and the acid soluble chlorides were determined by the potentiometric titration with silver nitrate [AASHTO T 260-97 [2005]]. Values for acid soluble chlorides concentrations are about 10 % higher than for the water soluble chloride concentrations.

Table 1. shows the chemical analysis results for Core 1.

Table 1. Acid soluble chloride concentration in Core 1 from 1 to 5 cm in depth [weight % of concrete]

Depth from surface [cm]	Chemical analysis wt. %
1	0.584
2	0.561
3	0.421
4	0.421
5	0.419

Concentrations of chlorides are quite high throughout the depth of 1 to 5 cm below the surface, i.e. to the vicinity of rebars. This implies that the transport of chlorides was through the cracks in concrete, rather than by diffusion. Table 2. shows both the acid soluble, as well as the water soluble chloride concentrations in Core 2, from 0.5 to 19.5 cm below the surface. The concentrations at the depth of 0.5 cm are as high as 0.577 % by weight of concrete [~ 15 kg chloride/m^3 concrete], and drop to barely detectable amounts at the bottom of the core. Concentration profiles are shown graphically in Figure 4. suggesting that the transport of chloride in an undamaged bridge deck sample is by diffusion.

Table 2. Acid soluble and water soluble concentrations of chloride in Core 2, from 0.5 cm to 19.5 cm from the surface [weight % of concrete].

Depth from surface [mm]	Water soluble chlorides	Acid soluble chlorides
5	0.525	0.577
15	0.434	0.468
25	0.312	0.341
35	0.191	0.213
45	0.138	0.152
55	0.106	0.136
65	0.114	0.148
75	0.072	0.104
85	0.088	0.114
95	0.088	0.102
105	0.079	0.106
115	0.078	0.081
125	0.066	0.07
135	0.044	0.056
145	0.038	0.044
155	0.031	0.034
165	0.02	0.022
175	0.008	0.012
185	0.009	0.019
195	0.01	0.01

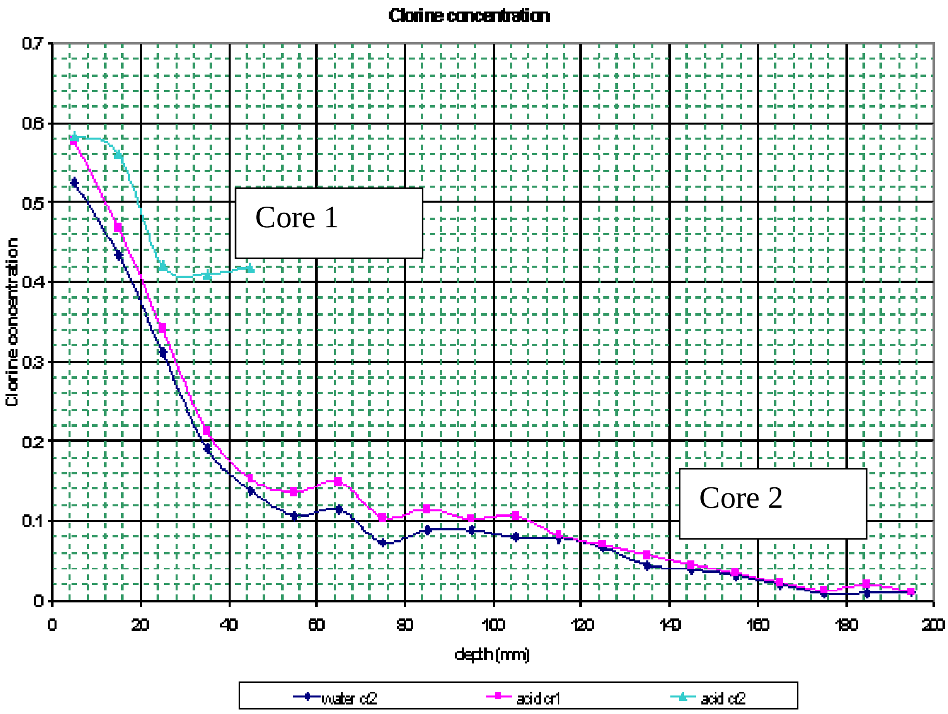

Figure 4. Chloride concentration profiles: Core 1 [green, acid soluble], Core 2 [purple, acid soluble; blue. water soluble].

Table 3. shows the comparison of the nominal concentrations and the chemically determined acid soluble concentrations in Rutgers' samples, showing a reasonable agreement.

Table 3. Acid soluble chloride concentration in Rutgers concrete samples:
Nominal vs. chemically determined [in weight % of concrete]

	Nominal wt. %	Chem. Analysis wt. %
Sample 0	0	0.01
Sample 100	0.03	0.03
Sample 500	0.15	0.11

2.2 NIR spectrometry results

There have been relatively few attempts to use spectrometric techniques to determine the chloride content on concrete. H. Wiggenhauser et al. report determining chloride content in concrete with a laser induced breakdown spectroscopy [LIBS] in the range above the 0.2 % of chloride by weight [2]. H. Kanada et al. used NIR spectroscopic imaging of concrete samples to determine chloride concentrations in cement paste as well as in the concrete samples [3]. A good agreement between their measurements and measurements done by traditional methods was achieved. M. Kohri et al. determined chloride content in mortar samples by means of NIR spectrometry. A good agreement between the chemically and spectrometrically obtained chloride concentrations was obtained [4].

In the work it was decided to test the applicability of readily available NIR instrumentation on real concrete samples, taken from bridge decks undergoing regular inspection and maintenance procedures. The chemical analysis left us some 30 powdered samples with known chloride concentrations. These samples were sent to two manufacturers of portable NIR spectrometers, which might be applicable to the field determination of chloride content in concrete structures. These were ASD Inc. from Boulder, Colorado and Brimrose Corp from Spark, Maryland. It was not certain that 30 samples will be enough to establish a viable correlation between the NIR and chemical measurements, but both teams were successful. Figure 5 shows a wt % chloride model developed by ASD Inc. Results are quite encouraging, indicating that NIR spectroscopic method might be capable of determining chloride concentrations over the whole range, from below 0.05 % by weight [considered below the threshold of corrosion] to quite high concentrations, exceeding 0.500 % by weight.

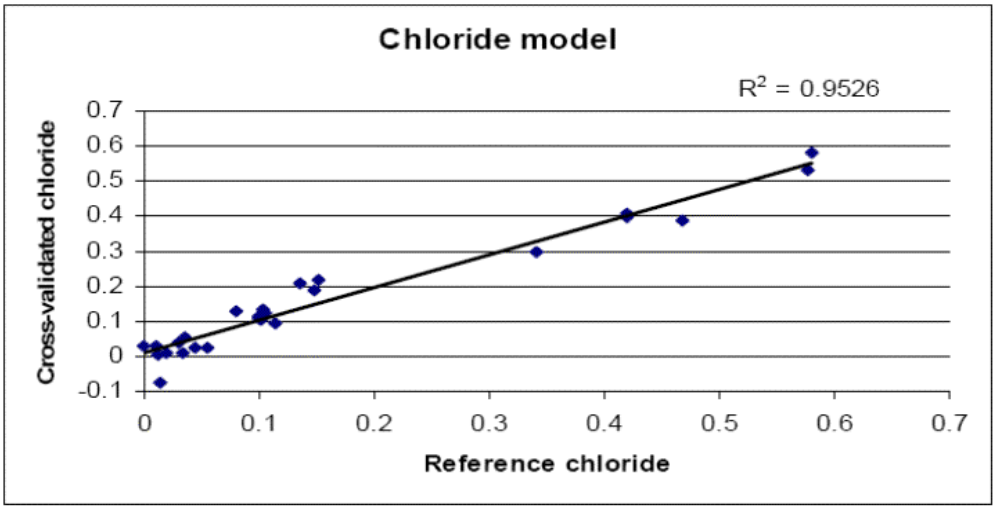

Figure 5. A chloride weight % model for predicting concentrations in concrete developed by ASD Inc. using 26 samples with known chloride concentrations.

A six sample validation set utilizing the developed samples showed very good agreement between the reference chloride and the predicted chloride concentration values- see Figure 6.

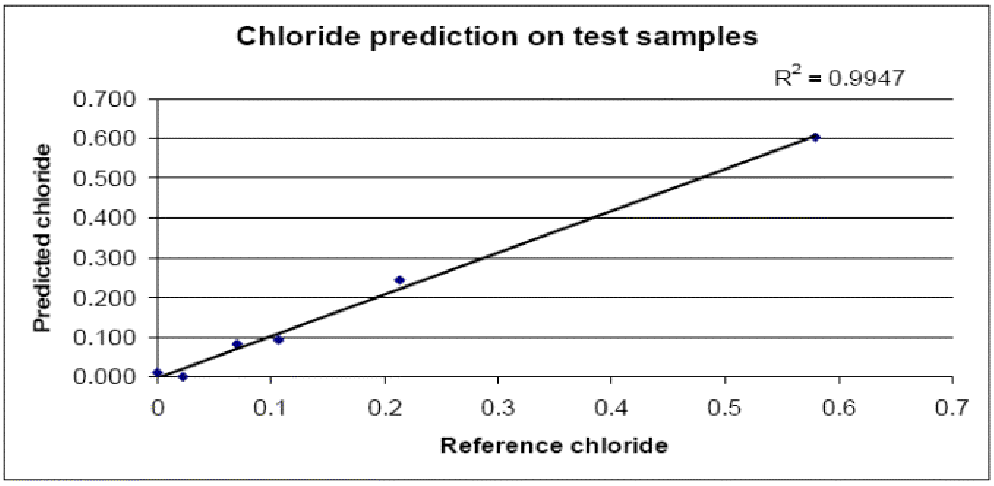

Figure 6. Chloride model validation set predictions based on 6 samples, ASD Inc.

Finally, a set of 10 "mystery " samples, with unknown concentrations was sent to both ASD Inc and Brimrose to test their NIR correlation models. Results of these analyses are given in Table 4.

Table 4. Comparison of chemical and NIR spectrometry determination of chloride concentrations [wt. % of concrete] on 10 samples

Sample No.	Chem. analysis	ASD Inc.	Brimrose
M1	0.577	0.563	0.656
M2	0.341	0.315	0.273
M3	0.213	0.234	0.178
M4	0.213	0.242	0.18
M5	0.152	0.198	0.172
M6	0.148	0.198	0.201
M7	0.106	0.126	0.062
M8	0.044	0.039	0.058
M9	0.035	0.049	0.051
M10	0.012	0	0.027

Results presented in Table 4 are quite encouraging [$R^2 > 0.95$], particularly since these are based on correlation models developed on a very limited number of samples. In most instances the chloride concentrations in concrete structures do not have to be determined with great precision, just the indication that the corrosion threshold at the rebar level has been reached or soon will be reached is usually sufficient to decide on the necessary maintenance steps.

3. CONCLUSIONS

NIR spectrometry is a very promising method for a rapid determination of chloride concentration profiles in concrete structures. Despite the limited number of samples, a reasonable correlation between the standard chemical and NIR measurements was obtained. It is likely that correlation models will be improved with more work to obtain an even better agreement. The plan is to analyze a wide range of samples based on different types of concrete and contamination levels to test the universality of the method. Finally, the method will be tested in the field with portable NIR spectrometers to asses its practicality.

4. ACKNOWLEDGEMENTS

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6. REFERENCES

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