

# Evaluating Corrosion in Concrete Structures by Measuring Chlorine Levels with Portable XRF Technology

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## Key Words

Bridges, concrete, rebar, corrosion, chlorine, inspection, Niton, XRF

## Goal

The goal of this note is to document the corrosion effect of chlorine in concrete structures, as well as illustrates the usefulness of portable XRF analyzers for rapid, accurate, on-site material inspection for structures such as bridges.

## Introduction

Chlorine-induced corrosion in such concrete structures as bridges is a major infrastructure problem because it weakens the steel reinforcement bar (rebar) embedded in the concrete, resulting in an overall weakening of the structure. Depending on the degree of corrosion, repair, rehab or total replacement of the structure may be required – significantly raising the total ownership costs.

In the corrosion process, chlorine-containing solutions penetrate through the cracks of the permeable concrete, reach the steel rebar, and induce corrosion reactions. (See related application note, “*Reinforcing the Service Life of Bridges with Portable XRF Analyzers.*”) The problem intensifies in marine areas and locations that are subject to de-icing agents.

The corrosion process may also impact other structural elements, such as the grout used to protect bridge cables. For example, elevated levels of chlorine (>0.08%, the specified limit) are suspected to threaten the life span of the Veterans’ Glass City Skyway Bridge in Toledo, Ohio.<sup>1</sup>

Monitoring the concrete in infrastructure for any premature signs of corrosive reactions is important to providing insight into life expectancy and total cost of ownership.

## Application

CA 2006 a report issued by the Center for Transportation Research and Education at Iowa State University, “Evaluation of Corrosion Resistance of Different Steel Reinforcement Types,” discusses the corrosion issue as it relates to an aging highway infrastructure. In particular, Section 2.2.4, “Chloride Ion Concentration Monitoring,” examines various evaluation methods.

“The AASHTO T 260-94 test (Sampling and Testing for Chloride-ion in Concrete and Concrete Raw Materials) suggests three procedures (Procedure A, B, and C) for determining the chloride ion content in concrete (Scannell and Sohaghpurwala 1996). Procedures A and B are time-consuming and complicated tests: Procedure A determines the chloride ion concentration by potentiometric titration, whereas Procedure B uses an atomic absorption process to determine the concentration of chloride ion. In Procedure C, the chloride ion concentration is determined using a specific ion probe.”

“An alternative to these three procedures is the nondestructive use of X-ray fluorescence (XRF) spectroscopy to analyze the chloride ion concentration in samples. XRF spectroscopy provides an analytical means to identify and quantify the concentration of elements contained in a solid, powdered, and liquid sample (Schlorholtz 1998)<sup>2</sup>”.



## Portable XRF Spectroscopy

XRF technology makes use of the ability to ionize elements by emitting low-power x-rays into the sample and then reading the returning fluorescent x-ray signal to determine the elements present along with their relative concentrations.

The handheld Thermo Scientific™ Niton™ XL3t GOLDD™+ XRF Analyzer offers a completely non-destructive method for elemental analysis. It is engineered to deliver low detection limits, uncompromised reliability, and rapid analysis. In addition, the Thermo Scientific geometrically optimized large area drift detector (GOLDD) technology brings lab-quality performance to portable XRF analyzers.

Providing up to 10 times faster measurement times than conventional technologies, it also provides the highest sensitivity and measurement accuracy, plus the capability of measuring light elements (magnesium, aluminum, silicon, phosphorus, and sulfur) without helium purge or vacuum. These instruments make it easy to perform trend analysis by averaging readings in real time or by downloading results later to a PC. These superior instruments offer key benefits:

- Instant chemistry for cement, grout, ore, rock, and drill chips
- Significantly fewer samples sent for external analysis
- Decision-making tools at your fingertips
- Instant, simultaneous chlorine analysis, plus 27 other elements
- Rapid analysis of impurity concentration

## Method

Concrete samples from the Cove Street Bridge, Middletown, Rhode Island were analyzed with the Niton XL3t GOLDD+ analyzer using Mining Calibration for various times, ranging from 70-120 seconds. The purpose of these measurements was to demonstrate that chlorine (Cl), along with other key elements, can be easily detected in the field, and thus provide valuable, quantitative information regarding existing or on-setting corrosion processes. Three separate tests were carried out, none of which required sample preparation.

- Cl content along a profile away from the surface
- Composition mapping of key elements
- Cl content in various distances from a crack

## Results

The Cl content was measured at five points along a 56 mm profile from the surface of the sample. As shown in Figure 1, there is a distinctive trend in the Cl content as testing moves away from the surface and deeper into the sample. The highest level of Cl is found near the surface (11.2%), drops sharply at about 20 mm away from the surface (1%), and levels at around a 30 mm depth (0.50%).

The usefulness of this information lies in the fact that when combined with the (known) Cl-corrosion thresholds for steel (0.2-0.4 %) it can be used to pinpoint specific bridge locations at which corrosion

levels have reached a dangerous threshold. Another way of using this type of measurement is by repeating it over time on the same spot on the bridge and gaining a better understanding of the corrosion rate at this particular site.

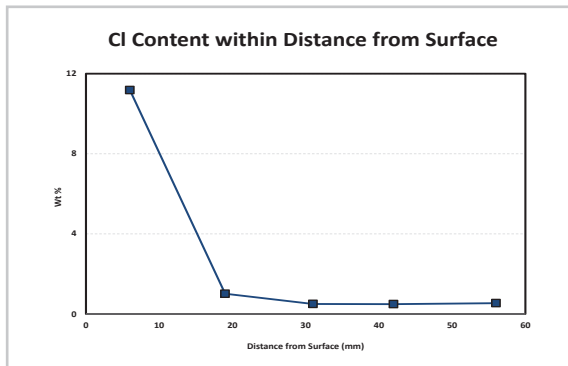
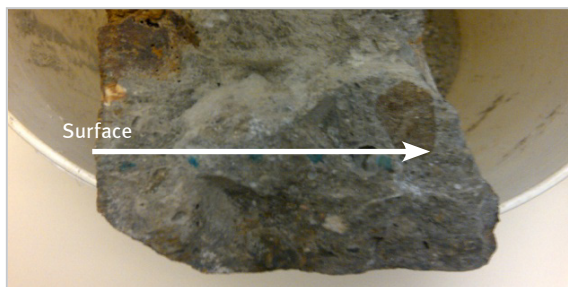


Figure 1: Cl content at various distances from surface

## Composition mapping of key elements

In the next set of measurements, the distribution of key elements (Ca, K, Al, Si, Cl, S) on the cement surface was measured in areas that showed four distinctive colorations, namely purple/brown, orange/brown, gray/yellow, and gray/white (see Figure 2). Accordingly, varying levels of certain elements and the co-existence of certain elements next to each other suggests the

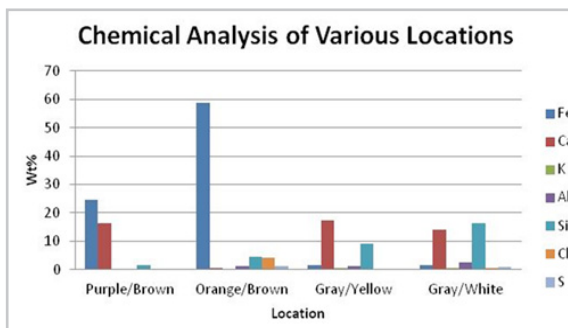


Figure 2. Chemical analysis of various locations on concrete sample

formation of various minerals, which, again, may be indicative of certain corrosion processes. For example, a high level of Fe (orange/brown areas) may indicate the existence of the mineral goethite. In another example, elevated levels of Ca and Si in the gray/white areas suggest the formation of calcium-silicates.

#### Chlorine content in various distances from a crack

In this part of the analysis, the Cl concentration was measured at various distances in relation to a 7 cm long crack. Interestingly, there is a clear dependence of the Cl level on distance from the crack (see Figure 3). The highest Cl level (almost 4%) was measured on the crack itself. Testing away from the crack, the Cl content drops to 2.9% and 1.5% at 2 cm and 11 cm away, respectively.

Without knowing whether the crack or the higher concentration of Cl was there first, the results from this test can be interpreted in various ways. One possibility is to assume that the crack came second, and use the Cl-concentration data as an early indicator for crack generation, and thus “forecast” new cracking sites (i.e. cracks are likely to appear at a Cl-concentration of 3-4%).

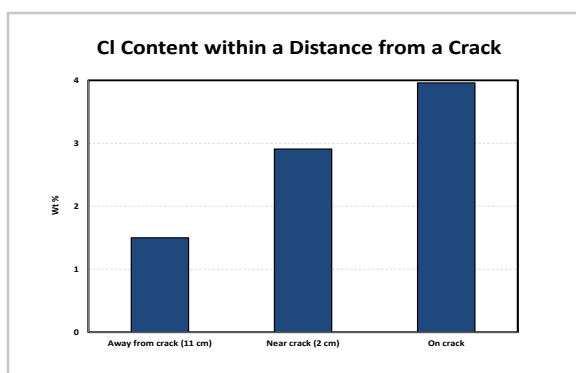
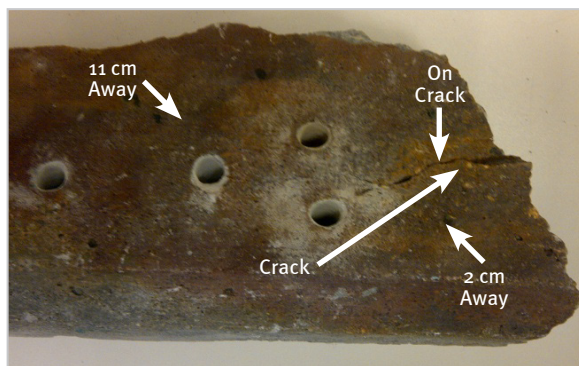


Figure 3. Chlorine content – various distances from a crack

#### Summary

The need to obtain accurate information about the chlorine content in cement structures such as bridges is critical for the early detection of any existing or on-setting corrosion processes. Portable XRF provides a robust field instrument that allows for on-site measurement while lowering outside lab analysis costs. It also minimizes downtime due to sample shipment and lab turnover time.

To discuss your particular application and performance

requirements, or to schedule an on-site demonstration, please contact your local Thermo Scientific portable XRF analyzer representative or contact us directly by email at [niton@thermofisher.com](mailto:niton@thermofisher.com), or visit our website at [www.thermoscientific.com/portableid](http://www.thermoscientific.com/portableid).

We would like to thank the Rhode Island Department of Transportation for its cooperation in gathering the data for this application note.

#### References

1. “Elevated Chloride Levels Found in Grout for Bridge Cables,” *Materials Performance Magazine*, March 2012, p. 8.
2. *Evaluation of Corrosion Resistance of Different Steel Reinforcement Types*: Final Report of the Center for Transportation Research and Education Iowa State University; sponsored by the Iowa Department of Transportation: Ames, Iowa, May 2006; pp. 8-9.

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