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Imaging the presence of silane coatings in concrete with micro X-ray fluorescence

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ABSTRACT

Silane is a commonly used surface treatment to reduce fluid entry into the concrete matrix. This work uses micro X-ray fluorescence (μXRF) to image the presence of silane coatings in field samples and the changes made to the paste chemistry. There are many advantages that μXRF has over other imaging techniques due to the large spot size and the high energy levels. Because of this, μXRF can rapidly investigate large areas and requires minimal sample preparation. Quantitative measurements are made to show that there is a reduction in the amount of sulfur and an increase in potassium in the hydrophobic regions formed by silane coatings. These measurements provide important insights into modifications made to the concrete matrix when silane sealers are used. The mechanisms for the observed chemistry changes are discussed and a simple field or laboratory test method is presented that uses a dye to detect silane coatings.

1. Introduction

Penetration of external fluids into concrete can lead to damage such as corrosion, alkali silica reaction, sulfate attack, bulk freezing and thawing damage, and scaling. The most prevalent and costly durability problem with structural concrete is the corrosion of internal reinforcing steel from chloride ions [1–5]. The chloride ions are typically contributed by deicing salts, ocean water, or from clays rich in ionic salts [6].

One cost effective method to extend the service life of concrete is to use protective coatings that decrease or eliminate the penetration of fluids. This is done by either lining the concrete pores with a waterproof surface, filling the pores, or a combination of these [7–10]. Organosilanes or silanes are commonly used to water-proof the pores. These are monomeric silicon-containing chemicals that contain at least one carbon-silicon bond. Silane molecules range from 10 to 15 Å in size and are typically dispersed in a solvent such as water or isopropyl alcohol that helps the silane penetrate into the concrete. The organic groups of the silane are bound to the silicon atoms by hydrolytically-stable carbon-silicon bonds and they result in coatings that are non-polar, have low surface energy, and are hydrophobic [11–15]. These coatings are advantageous because they line pores and make them hydrophobic providing a barrier to ingress of water but allowing vapor in or out of the concrete. As vapor is allowed to leave the concrete, the internal moisture of the concrete is thought to decrease over time.

Currently, an evaluation of silane long-term in-service performance is an important challenge for engineers [16]. It has been reported that a silane long-term performance is related to silane penetration depth into the concrete and the amount of silane active ingredient [12,17–19]. One appropriate method for evaluation of silane long-term durability is the investigation of in-service concrete to determine a silane effective depth. Currently, the determination of the depth of penetration of the silane coating represents an analytical challenge [19]. While some staining and optical techniques are used on concrete, they are challenging to interpret and require judgment. One solution is to use a rapid imaging or depth profiling analytical method. This ability to use the chemistry and spatial distribution information is helpful to reliably determine the silane penetration depth.

Scanning electron microscopy – electron dispersive spectrometry (SEM – EDS), electron probe microanalysis (EPMA), Auger electron spectroscopy (AES), and X-ray photoelectron spectroscopy (XPS) are some of well-known surface techniques in characterizing the surface chemistry of the cementitious materials [20–22]. However, these techniques have intrinsic limitations [21–23]. Another useful technique to image surface chemistry of cementitious systems is time-of flight secondary ion mass spectrometry (ToF-SIMS). This technique ionizes samples and then detects the elemental concentration by the time-of-flight from the sample surface to the detector [22,24]. Unfortunately, the method requires extensive sample preparation and the measured

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Table 1
Summary of μXRF settings used.

Parameter	Value
Counts per second	Minimum of 20,000
Current	1 mA
Dead time	Maximum of 20%
Dwell time	400 ms/pixel
Filter	25 μm Al
Vacuum	1.35 TORR
Voltage	40 keV

intensities are not directly proportional to the concentrations and so the analysis is semi quantitative [22].

This work describes the use of micro X-ray fluorescence (μXRF) to non-destructively analyze silane-coated concrete. This technique is similar to bulk X-ray fluorescence (XRF) but this method uses a polycapillary optic to focus X-rays to a size of approximately 50 μm in diameter, whereas bulk XRF investigates the sample with a 1 cm diameter spot.

μXRF has many advantages over electron based imaging techniques such as SEM – EDS or EPMA [23,25–26]. X-rays interact more weakly with matter than electrons and so they penetrate deeper into the sample (up to1 mm for X-rays compared to a few microns for electrons) [23, 27]. This deeper penetration makes the results less sensitive to the surface roughness. Furthermore, μXRF does not require conductive coatings to reduce electron build up or charging [28–29].

Previous publications have used μXRF to investigate ions infiltration into the cement-based materials [23,25–26,29–32]. The presented work implements μXRF to image the presence of silane coatings in concrete. One principal advantage of μXRF is the ability to determine the effect that silane has on the overall composition of the cement paste. This technique is then used to validate a simple and inexpensive visual dye method to determine silane location. Finally, X-ray diffraction (XRD) was used on powder samples which were collected with and without silane present to discern any differences.

2. Experimental procedure

2.1. Sample acquisition and preparation

Cylindrical samples approximately 12.5 mm diameter and 25 mm height were taken from various in-service bridge decks in Oklahoma, United States. These bridges had been treated with silane within a year of construction with a specified depth of penetration of 3.2 mm [33]. These bridges had an age range of 5 to 20 years. Although individual mixture designs and commercial silane used varied, all of them were constructed to known specifications [33]. The mixture design of the bridges had maximum water to binder ratio of 0.42, a minimum cement content of 335 kg/m^3 and typically only contained portland cement as a binder. All approved silane sealers are alcohol based and used between

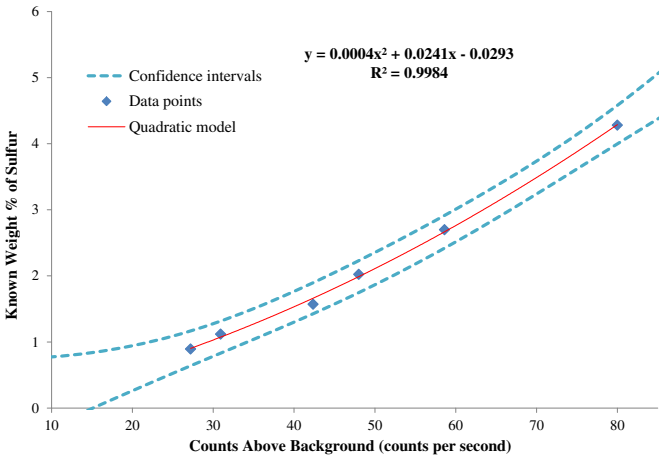

Fig. 2. Sulfur calibration curve used to change from counts to weight percentage in the μXRF analysis.

40% and 50% active ingredient and were treated within a year of construction [33–34]. Two representative samples with and without silane sealers are presented. Additional examples are included in the supplementary section. More details can be found in other publications [35].

Before testing, each sample was polished with 120 grit sand paper for 300 s to prepare a flat surface. This surface preparation is necessary to remove the saw marks and reduce surface roughness to improve the quality of the μXRF and optical images. Finally, ethanol was used to remove grinding debris and residue from the polished surface.

2.2. Methods

2.2.1. μXRF

Investigation of the samples was conducted using an Orbis μXRF by EDAX, equipped with an 80 mm^2 Silicon Drift Detector Energy Dispersive Spectrometer (SDD-EDS). μXRF uses polycapillary optic to focus X-rays to a spot size of approximately 50 μm in diameter. Images are created by moving the sample in a raster pattern under a stationary X-ray beam. These images are sensitive to trace (0.1% by weight or lower) level elements, and they are ideal for tracking small changes in chemistry. When the focused beam is addressed to the sample, characteristic fluorescence X-rays are emitted, the intensity of which are measured by the SDD-EDS and stored in a database for later processing and analysis. Table 1 contains a summary of the μXRF settings used.

Sufficient count data is necessary to perform an accurate compositional analysis. A minimum of 8000 integrated counts at each pixel were required for adequate data for silicon, sulfur and chloride analyses. Unfortunately, these important elements have relatively low count rates. At an overall count rate of 20,000 counts per second, a 400 ms dwell time at each pixel was found to be satisfactory. An accelerating

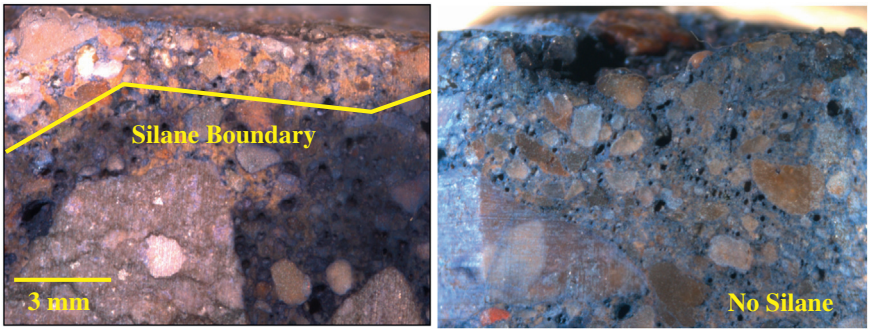

Fig. 1. Finding the presence of silane through visual contrast through ponding cores in blue dye. (Left) core showing evidence of the presence of silane (right) core showing no evidence of the presence of silane. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)