

INVESTIGATION OF SILANE TREATMENTS IN  
CONCRETE USING VARIOUS NON-DESTRUCTIVE  
TECHNIQUES

By

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Abstract:

Silane is commonly used on bridge decks to reduce water entry into the concrete matrix by lining pores with a hydrophobic film. This work establishes and evaluates some important non-destructive laboratory and field techniques that can be used to determine the presence and effective lifespan of silane treatments. A review of existing literature is given in order to provide a thorough understanding of silane treatments. From here, four different non-destructive techniques are investigated including Micro X-ray Fluorescence ( $\mu$ -XRF), the 4-Point Wenner Probe, a brominated-dye, and a chlorine-based dye. All four techniques are then compared to determine which technique is most effective in determining the presence and depth of penetration of silane in concrete. Finally, by using this technique recommendations are provided to outline the useful service life of silane as well as the ability to reapply this material.

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## CHAPTER I

### INTRODUCTION

Concrete structures face a multitude of problems that threaten the serviceability of the structure, one of the largest being chloride ingress. The chlorides permeate through the concrete matrix causing corrosion of the steel reinforcement. According to a study conducted by the Federal Highway Administration (FHWA), the total direct cost of corrosion from 26 analyzed sectors was determined to be \$279 billion per year in the United States. Of this total, it was estimated that \$8.3 billion in damages occurred specifically to highway bridges [Koch, 2001].

One cost effective method to prevent chloride ingress is the use of protective coatings. These coatings stop chloride ingress by either clogging the pores of the matrix thus reducing the material that permeates into the concrete, or by lining the concrete pores with a water repellent coating. An example of the latter is organosilane or silane. Silane is used by the state of Oklahoma and many others to prolong the service life of bridge decks. Currently, no published literature exists that has determined the useful service life of silane treatments or the ability to reapply this material.

The focus of this thesis will be to establish and evaluate some important non-destructive laboratory and field techniques that can be used to determine the presence and effective lifespan of silane treatments. In Chapter 2 a review of existing literature was given in order to provide a thorough understanding of silane treatments. From here, four different non-destructive techniques

were investigated. In chapter 3 an experimental laboratory technique called Micro X-ray Fluorescence ( $\mu$ -XRF) was investigated and in chapter 4 three field techniques including the 4-Point Wenner Probe, a brominated-dye, and a chlorine-based dye were investigated. In chapter 5 all four techniques were compared to determine which technique is most effective in determining the presence and depth of penetration of silane in concrete. Finally, by using this technique recommendations are provided to outline the useful service life of silane as well as the ability to reapply this material.

## CHAPTER II

### REVIEW OF LITERATURE

This document covers the basics of surface treatments and provides an overview of silane, including a brief history, definition, and applications. Finally, with an understanding of basic principles in place, the chemistry of the interaction between the substrate and silane treatment are explored in detail.

#### **2.1 Damaging Effects of Water Penetration**

Penetration of water into concrete can lead to damage such as staining, corrosion, organic decay, bulk freezing and thawing, and scaling [Basham, 1995]. In particular, chloride ingress due to capillary suction or diffusion is one of the biggest causes of corrosion of the reinforcement in concrete structures. Chloride ingress happens through water transport, especially in high brine areas from deicing salts, salt water or spray from the ocean, and occasionally from soils. One useful and economical technique to suppress chloride ingress into concrete is the use of surface coatings on concrete.

#### **2.2 Types of Surface Treatments**

Surface treatments are categorized into several general classifications: penetrating sealers, surface sealers, high-build coatings, membranes, and overlays [ACI 546, 1981]. They are composed of binders and fillers; and cure by one of the following methods: evaporation of a solvent or

dispersant (e.g. water or alcohol), a chemical reaction with a catalyst, a reaction with moisture in the atmosphere or concrete substrate, or a reaction with oxygen in the atmosphere. The performance of these treatments is very sensitive to the components in the filers.

Surface treatments protect the concrete substrate by slowing down or eliminating the penetration of water and ions in the water (e.g. chlorides). This is done by one of two means: lining the pores in the concrete which reduces the surface energy, or by penetrating the pores and reacting with some of the concrete constituents and depositing products that block the pores. [Bentur, 1997; Kamel, 1993; Schueremans, 1997].

### **2.2.1 Penetrating Sealers**

Penetrating sealers are generally low viscosity liquids that penetrate at least 6 mm into the concrete substrate and line the pores. The depth of penetration depends on two things: the size of the sealer molecule and the size of the pore structure in the concrete substrate. They are colorless, hydrophobic, have good ultraviolet and abrasion resistance, and do not block pores (i.e. allow vapor transmission). On the other hand, penetrating sealers are sensitive to contaminants and previously applied sealers, and will not bridge new or existing cracks. Most penetrants are based on silanes, siloxanes, or silicone resins and can be applied by using a roller, squeegee, or spraying [ACI 546, 1981; Attanayaka, 2002; McGill, 1990].

For more information on surface treatments, including silane and siloxane, and/or the preparation process before applying treatments see [ACI 515, 1985; ACI 546, 1981; Kosmatka, 1997].

### **2.3 Methods of Silane Adhesion**

There are three different mechanisms through which silane treatments can adhere to a surface.

These include mechanical adhesion where the sealer “grabs hold of” the rough or uneven surface of the substrate, hydrogen bonding, and covalent bonding [Stoffer, 1989].

## 2.4 Assessment Methods for Surface Treatment Effectiveness

Surface treatments are evaluated based on several properties including transport processes in the treated substrate, durability of the treated substrate, durability of the surface treatment, influence of the substrate properties, engineering requirements, economic requirements, and service performance [ACI 515, 1985; Basheer, 1997].

Water and water vapor absorption are two of the most important transport processes to consider for concrete. Water vapor permeability/diffusion can be tested by one of the following methods: water-absorption-desorption method, or dry-cup/wet-cup method. Results from various lab tests indicate that silicon based treatments such as silanes and siloxanes are as permeable to water vapor as untreated concrete [Basheer, 1997; Kamel, 1993]. However, they are quite resistant to the penetration of moisture. The quality and condition of the treated substrate can have a significant impact on the performance of the surface treatment. Durability of the treated substrate should improve resistance to several deterioration mechanisms including corrosion due to chloride ingress, sulphate ingress, freeze thaw deterioration, and salt scaling [Basheer, 1997; Kamel, 1993].

Additional performance characteristics of the sealer to consider include: water and vapor permeability, penetration depth, ultraviolet resistance, skid resistance, resistance to external sources of alkalis, crack bridging, reactivity of the concrete materials, and appearance [ACI 546, 1981; Basheer, 1997; Kamel, 1993; Kosmatka, 1997; Salt Institute, 2006; Schueremans, 1997].

A number of test methods have been used to investigate the performance and evaluate the effect of surface treatments on concrete durability including:

- AASHTO T 259/260 test [Kamel, 1993; ODOT, 1986; Pincheira, 2005; Wenzlick, 2007]
- AASHTO T 277 [Kamel, 1993; Wenzlick, 2007]
- Alberta Transportation and Utilities (AT&U) Sealer Test Method [Carter, 1994]

- ASTM C 642 [Kamel, 1993; ODOT, 1986; Wenzlick, 2007]
- ASTM C 672 [Wenzlick, 2007]
- ASTM C 1202 rapid permeability test [Pincheira, 2005]
- ASTM C 1293 test [Eskridge, 2004]
- Dye Method [Pincheira, 2005]
- Electron microscope [ODOT, 1986]
- NCHRP 244 Series II test [Kamel, 1993; Pfeifer, 1996; Wehrle, 2010]
- ODOT Test Procedure L-34 [Kamel, 1993; ODOT, 1986] and L-35 [Kamel, 1993; ODOT, 1986]
- Ohio Modified T 259 test [Wenzlick, 2007]
- OHP L-40 test [Kamel, 1993; Pincheira, 2005]

Evaluation of the relative performance of sealers in the field can also be tested using the electrical resistivity method, which is used to measure surface resistivity that indicates the functioning of sealers as hydrophobic agents. There are many modified electrical resistivity methods, but the most common method is the Wenner four-probe resistivity measurement method [Attanayaka, 2002].

## **2.5 Basic Information on Silane**

### **2.5.1 History of Silanes**

Organosilicon compounds have been known since 1863 when Friedel and Crafts first reported the synthesis of tetraethylsilane from diethylzinc and silicon tetrachloride. Before 1982, alkoxysilanes were produced from chlorosilanes and alcohols which produce hydrochloric acid as a by-product. In 1982, tetramethoxysilane (TMOS) could be made directly from elemental silicon and methanol; which means alcohols are now produced as a by-product instead of the hydrochloric acid produced manufacturing siloxanes [Stoffer, 1988].

## 2.5.2 Silanes and Siloxanes

Currently commercially available water repellents contain a carrier such as alcohol and can be classified according to their active ingredient content by weight, up to 100%. Performance is reported to increase with an increase in solids content. Most siloxane-based water repellents have much less than 10% active ingredient, while available silanes may have 40% active ingredient. Both silanes and siloxanes can be effective as crack sealants for crack widths less than 0.05 mm (hairline cracks). Silanes have a smaller molecular size than siloxane, which allows for better penetration into dry substrates [Attanayaka, 2002; Kosmatka, 1997]. When evaluating the effectiveness of a silane, it is found that a combination of the amount of active ingredient and the ability for that material to penetrate into the concrete that is responsible for long term performance.

### 2.5.2.1 Silane

Silanes are monomeric silicon chemicals that contain one carbon-silicon bond structure called an organosilane. Silane molecules range from 10-15 Å in size. The carbon-silicon bond structure is very stable, very non-polar, and gives rise to low surface energy, non-polar, hydrophobic effects. Silanes also contain a silicon-hydride (-Si-H) structure that is very reactive with water, which produces silanols (-Si-OH). A secondary group (e.g. methoxy) that is attached to the silicon gives a very reactive and hydrolysable structure [Anderson, 1987; Attanayaka, 2002; Dow Corning, 2005; Petrie, 2007].

There are two basic classifications of alkoxy silanes: alkyl/aryl and organofunctional. There are no naturally occurring organosilanes, but they can be derived from what is known as the Direct Process (a.k.a. Rochow Process). The most common usage of this reaction is the formation of dimethyldichlorosilane. Byproducts from this process are used to prepare several other organosilanes including methyltrichlorosilane and trimethylchlorosilane [Anderson, 1987].

### **2.5.2.2 Siloxanes**

Siloxanes are oligomeric (chained molecular structures) alkylalkoxysiloxanes that have the same advantages as silane in respect to reactivity and water repellency, but have low vapor pressure. Under dry conditions, they exhibit slightly less penetration than silanes. Whereas silanes have only one silicon atom, siloxanes have more than one silicon atom and a molecular size from 25-75 Å [Attanayaka, 2002; McGill, 1990].

### **2.5.3 Silylation**

Silylation is when a chloro, alkoxy, acetoxy-silanes, and siloxanes, react with active hydrogen on an organic chemical. This protects functional groups while other chemical manipulations are being performed, and the process can be reversed to convert back to the original organofunctional groups afterwards [Dow Corning, 2005].

## **2.6 Chemistry of Organofunctional Alkoxy Silanes**

Alkoxy silanes are the most common commercial adhesion promoters and are commonly used to enhance the adhesion between polymeric and inorganic materials. They contain two types of reactivity in the same molecule: an inorganic and an organic reactivity. This combination allows the silane to act as a bridge at the interface of an inorganic substrate and an organic material to bond the two dissimilar materials together [Dow Corning, 2005; Petrie, 2007].

Benefits from using silane coupling agents include increased strength and humidity resistance of coatings and adhesives, better wetting of inorganic substrates, lower viscosities during compounding, smoother surfaces of composites, less catalyst inhibition of thermoset composites, clearer reinforced plastics, and an interphase region that is more resistant to chemical attack from the surrounding environment [Dow Corning, 2005; Petrie, 2007].

The general formula for an organofunctional alkoxy silane is:



Organofunctional alkoxy silanes contain two functionality classes, an organofunctional class (-R end) and a silicon functional class (-X group). The organofunctional class is a non-hydrolysable organic radical (e.g. vinyl, amino, chloro, epoxy, mercapto, etc.) that possesses a functionality which enables the coupling agent to bond with the organic resins and polymers. The organofunctional group provides the hydrophobicity of the treatment. The X group is a hydrolysable group (e.g. alkoxy, methoxy, ethoxy) that is involved in the reaction with the inorganic substrate and reacts with water to form silanol groups [Anderson, 1987; Kamel, 1993]. These silanols can react with other silanols as well as active surfaces that contain hydroxyl groups to form oligomeric variations and an oxane bond with the inorganic substrate, which liberates methanol or ethanol as a by-product [Anderson, 1987; Petrie, 2007]. These reactions between silanols with other silanols (or with hydroxyl groups) form very stable bonds that contribute towards inter-particle bonding and allow silanes to function as valuable surface-treatments and coupling agents [Anderson, 1987; Dow Corning, 2005; Liles, 1991; Petrie, 2007].

The reaction process between the coupling agent and the substrate can be broken down into four basic steps:

1. Hydrolysis
2. Condensation
3. Hydrogen Bonding
4. Bond Formation

The rate of the entire reaction process is determined by the rate of hydrolysis [Oostendorp, 1985; Stoffer, 1988] and the relative acidity/basicity (pH) of the interface [McGill, 1990; Petrie, 2007].

## **2.6.1 Hydrolysis**

Hydrolysis is the chemical decomposition in which a compound is split into other compounds by reacting with water. In the case of silanes, hydrolysis of the three labile X groups attached to silicon occurs. They are usually hydrolyzed to silanetriols before coming into contact with the substrate [Anderson, 1987; Stoffer, 1989]. Hydrolysis is required for interactions to occur between organosilanes and various inorganic materials and may require an acid or base catalyst [Oostendorp, 1985; Petrie, 2007; Pohl, 1985]. It is important to understand that the organosilane hydrolysis must be controlled in ways that correspond in size/degree with both the end-use application and process [Petrie, 2007].

### **2.6.1.1 Hydrolysis of Alkyltrialkoxysilanes in Aqueous Solutions**

Hydrolysis of alkyltrialkoxysilanes in aqueous solutions occurs in a step-wise manner; where the first step is the slowest and produces silanols, the second step produces silandiols, and the third step produces silanetriols [Pohl, 1985].

## **2.6.2 Condensation**

During this step, silanol molecules condense to oligomers which are molecules that contain a few monomers [Anderson, 1987; Petrie, 2007].

## **2.6.3 Hydrogen Bonding**

The oligomers will then hydrogen bond with hydrocarbon molecules (i.e. OH groups) of the substrate, which reduces the surface tension of substrate to less than that of water [Anderson, 1987; Kamel, 1993; ODOT, 1986]. Hydrogen bonding is also believed to be significant in inter-particle adhesion [Liles, 1991].

#### 2.6.4 Bond Formation

During curing, covalent bonds form with the substrate with a naturally accompanying loss of water. At the interface, there is usually only one bond from each silicon molecule to the organosilane to the substrate surface. The two remaining silanol groups are present either as bonded to other coupling agent silicon atoms or in free form [Anderson, 1987].

The bonding mechanism depends on several factors including the relative acidity/basicity (pH) of the interface, thermodynamic compatibility of the polymer with the organosilane and its condensation products, temperature dependence of hydrolysis and condensation, temperature dependence of the polymer interpenetration, and the activation energy for achieving a covalent bond. It is important that the chemistry of the organosilane and the base polymer be matched for optimum properties [Petrie, 2007]. In the case of concrete, it is important to note that the high alkalinity of the pore solution in the concrete (i.e. pH=13-13.5) can result in breaking the bond between the silane molecules and the substrate; however, this reaction can be avoided by using silane with branched iso-octyl or iso-butyl alkyl groups [Kamel, 1993].

The bond formation also depends upon characteristics of the substrate. First, organosilanes form strongly adsorbed films on inorganic surfaces, of which the integrity of these films is highly dependent on the chemical and physical character of the substrate. Secondly, organosilane adhesion promoters are not generally applicable for bonding surfaces that are devoid of active hydroxyl functionality. Last, smooth, high energy substrates are excellent for organosilane attachment, and rough, discontinuous substrates show very little benefit [Petrie, 2007].

The physical properties of the interphase region of the joint will depend on the properties of the substrate adhesive and organosilane additive. A soft interphase could significantly improve fatigue, thermal cycling, and reduce internal joint stress concentrations. A rigid interphase will

improve stress transfer of resin to the adherent and improves interfacial shear strength [Petrie, 2007].

Molecular arrangement of the silanes occurs in layers with a high degree of order, which is greatly influenced by the surface of the substrate. The molecules order themselves perpendicularly to the surface to which they attach; and subsequent layers arrange themselves step-like in a head-to-head fashion. It is important to understand that a rough surface can break up the first ordered layer preventing the formation of the second [Petrie, 2007].

## **2.7 Applications of Silanes**

Applications of silanes include water repellent surface treatments, moisture scavenger, increasing the physical strength of different compounds, improving the dispersion of fillers or minerals [Dow Corning, 2005], additive to paints, inks, resins, polymers, and adhesives [Dow Corning, 2005; Petrie, 2007], a reactive intermediate for silicon resin synthesis and organic resin modification [Witucki, 1993], adhesion promoter or coupling agents [Bone, 1991; Dow Corning, 2005; Oostendorp, 1985], crosslinking agent, silicate stabilizer, fiberglass, composites, plastics and rubber, improving electrical properties of materials, polypropylene catalyst “donor”, and pharmaceutical manufacturing [Dow Corning, 2005].

The two main applications of alkoxy silanes include water repellent surface treatments and adhesion promoter/coupling agents. Additional advantages of both silanes and siloxanes include no discoloration of the concrete and no reduction of the coefficient of friction [Kamel, 1993; Kosmatka, 1997].

### **2.7.1 Surface Treatments**

Alkoxy silanes can be applied to material surfaces (e.g. natural stone, concrete, and brick) to provide a hydrophobic (or sometimes an oleophobic) surface sealant [Dow Corning, 2005].

Silanes chemically bond to concrete, which is a much stronger type of bond than adhesion or physical bonding, but do not significantly affect pavement surface friction after evaporation [ODOT, 1986]. It can provide many benefits to concrete such as excellent water repellency, long term durability, UV stability, water vapor permeability, high dilution capacity and stability, reduced efflorescence, reduced freeze-thaw damage, chloride ion resistance to deter corrosion of the reinforcing steel, chemical and thermal resistance, and clear, uniform, neutral appearance as well as preserving aesthetics. In addition, silanes contain only 10g VOC/liter which are well below current regulations [Dow Corning, 2005; Kamel, 1993; ODOT, 1986; Pfeifer, 1996; Standke, 2005; Stark, 1992]. Water repellents must penetrate as deep as possible into the concrete substrate in order to obtain long-term performance. Several factors affect the penetration capacity of water repellents including molecular size of active organo-silicon compounds (e.g. silane molecules are about x1000 smaller than the average capillary pore diameter in concrete), type and solvent used for dilution, the porosity, permeability, and water content of the concrete substrate, as well as the amount of the water repellent material applied. The action of capillary forces is the main factor that provides a high absorption rate of the silane into concrete, which normally exceeds that rate of evaporation [Carter, 1994; Kamel, 1993; Schueremans, 1997].

Silane penetration depth and waterproofing effectiveness generally improve as the permeability and water-cement ratio of concrete decreases. The reason for this could be that a reduced volume of pore space may simply reduce internal surface area that is coated, therefore allowing non-reacted silane to penetrate deeper [Carter, 1994; Kamel, 1993; Kosmatka, 1997].

In addition to mixture design properties, the performance of silane can be affected by curing and cleaning procedures. Silane can be adversely affected when applied to existing structures that have been previously treated with compounds such as pigmented membrane curing compounds [Kamel, 1993]. If these curing compounds are removed or allowed to wear off then this greatly aids in the effectiveness of the sealer penetration.

Silanes can also be applied to wet concrete, but dry concrete is preferred in order to facilitate better penetration into the pores [Bentur, 1997; Kamel, 1993; ODOT, 1986]. They are usually dissolved in a carrier to insure equal distribution over the area where treatment is intended, but they do not need to be diluted with alcohol. Silanes can be diluted with water but will form a condensed, unstable gel when stored for some time. The solution reaction within concrete is a delicate balance. Not enough of the hydrophilic surface creates an unstable condition, but too much creates a poor water repellent material [Carter, 1994; Kamel, 1993; Stark, 1992].

Testing has shown that on average, solvent-based silane products penetrate deeper and are generally able to reduce the ingress of chloride ions better than water-based silane or siloxane products [Pincheira, 2005]. Surfaces previously treated can be retreated with silane, and the depth of penetration generally improves if the concrete has had sufficient time to dry [Carter, 1994; Kosmatka, 1997]. Although little work has been done with mature concrete, this is a focus of this research. Additional testing has shown that silane can be applied over appearance paint and still reduce internal relative humidity and expansion, which can help reduce deterioration mechanisms like alkali-silica reaction and delayed ettringite formation [Wehrle, 2010]. Other work has shown that certain combinations of silanes with other additives can prevent or retard surface cracking by preventing rapid moisture loss from the surface [Eskridge, 2004].

### **2.7.2 Methods to Apply Silanes to Concrete Surfaces**

Several concerns have been brought up about the difficulty of applying silane treatments in the field including that silanes “slide off” when applying, the preparation recommendations (i.e. dry, clean concrete) are impractical, penetration is poor, impossible to spray, not compatible with current biodegradable curing compounds, and that there is no proof/information on the long term durability of the silane treatments. Despite these concerns, experts claim that silanes retain their water repellent properties after being subjected to artificial weathering and salt spray tests; while

siloxanes do not retain their water repellent properties, which requires reapplication more frequently, which in turn will ultimately cost more [Alexander, 1991; Robery, 1991]. For guidance on silane application see ACI 546.

## CHAPTER III

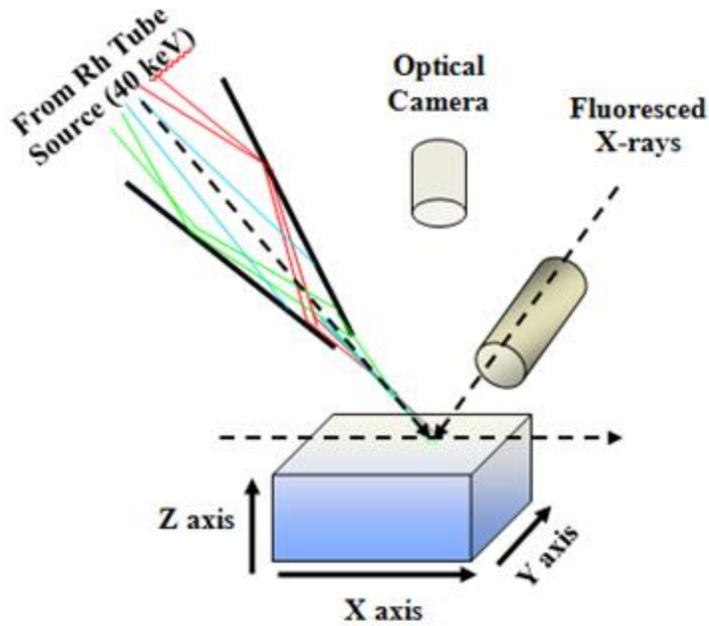
### USING MICRO X-RAY FLUORESCENCE TO INVESTIGATE SILANE IN CONCRETE

#### **3.1 Overview**

This work discusses the use of an experimental method called Micro X-ray Fluorescence ( $\mu$ -XRF) that was used to investigate silane that has been in service in bridges from 5-25 years to determine the presence and effectiveness of the silane layer.

#### **3.2 Micro X-ray Fluorescence ( $\mu$ -XRF)**

Micro X-ray Fluorescence ( $\mu$ -XRF) is a non-destructive, microanalysis technique that uses an x-ray optic to focus a stationary beam of x-rays onto a sample to perform a chemical composition analysis as shown in Figure 1.

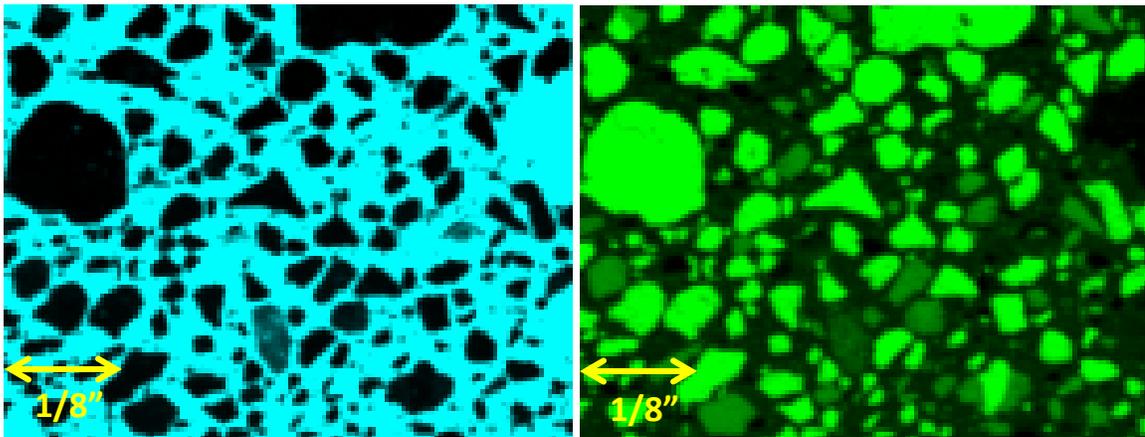


**Figure 1:** A diagram of a typical  $\mu$ -XRF setup.

X-rays are capable of deeper penetration than charged particles or electrons as is commonly used with scanning electron microscopes (SEMs). Because of the deeper penetration of X-rays more information can be identified from deeper within the concrete matrix. Because of this deeper penetration, sample preparation becomes less tedious when using x-rays as opposed to charged particles; therefore obtaining a smooth, flat surface is not as critical and using conductive coatings like gold and carbon are not necessary. Finally, with  $\mu$ -XRF the process can be automated and the scan can be performed under a light vacuum.

Whereas conventional XRF (or Bulk XRF) targets x-rays at a sample with an approximate spot size of 1 cm,  $\mu$ -XRF uses an x-ray optic to focus x-rays down to a spot size of 50  $\mu\text{m}$ . By focusing the x-rays to a smaller spot size, analysis of much smaller features on the sample surface becomes possible. In addition, unlike Bulk XRF which only provides a summary of the chemical composition,  $\mu$ -XRF is able to produce chemical composition maps with ppm-level sensitivity that describes the location and intensity of chemical components.

Upon focusing the beam of x-rays, the sample will absorb the x-rays and emit a fluoresced x-ray. The fluoresced x-ray intensities are then assigned as pixels into an image. The brighter the pixel in the image is, the greater the intensity of the fluorescing x-rays. Each element will emit a unique signal allowing maps to be produced of different element concentrations, like those shown in Figure 2. The concrete sample shown in Figure 2, demonstrates the  $\mu$ -XRF ability to provide information on both the aggregates and the cement paste. The calcium map on the left shows that, for this particular sample, the majority of the calcium content exists within the cement paste. Likewise, the silicon map on the right shows that the majority of the aggregates in the sample are highly siliceous.

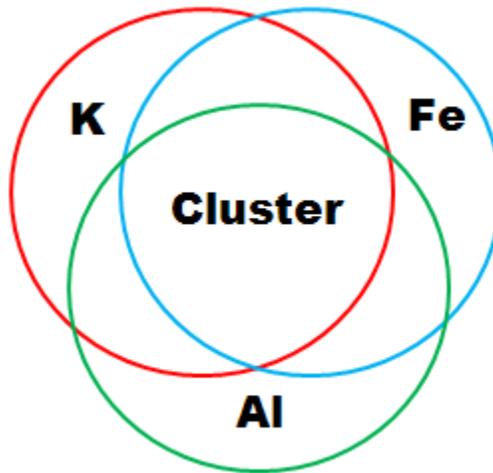


**Figure 2:** (left) elemental calcium image and (right) elemental silicon image.

### 3.3 Cluster Analysis

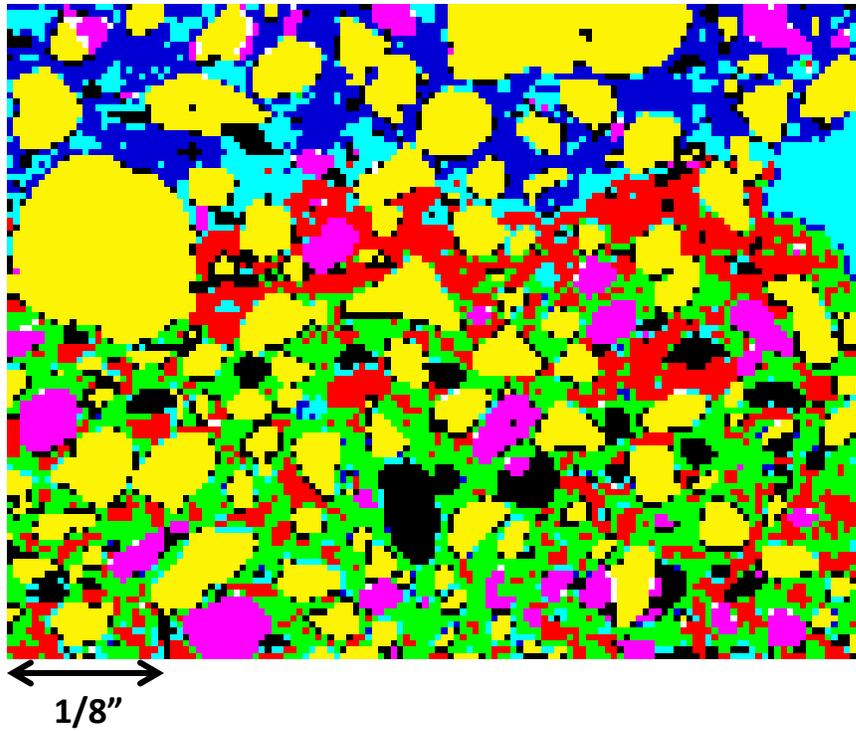
These chemical maps are then analyzed with an image processing software package by means of a composition analysis called cluster analysis. Cluster analysis is a means to identify the surface of the scanned sample by grouping areas that have a similar chemical composition into a cluster. This analysis provides valuable information such as the chemical composition of the cluster, the location of the component, and the total amount of those components.

Clusters are developed by selecting areas of high concentration on the sample and then identifying areas of unique chemical makeup. Since an area will most likely consist of multiple elements, the cluster will consist of the area of overlap of all elements in consideration for the given cluster, as shown in Figure 3.



**Figure 3:** A cluster defined by aluminum, iron, and potassium.

This process is repeated until the entire surface has been defined (i.e. multiple clusters). Then a cluster map, like that shown in Figure 4, is produced which combines all individual clusters into a single image where each color in the cluster map represents a separate cluster. The yellow and magenta clusters in Figure 4 represent two different types of aggregates; whereas the light and dark blues, red, and green clusters represent cement paste that has been segmented based on varying levels of sulfur concentrations. Table 1 gives a summary of the different colors contained in Figure 4.



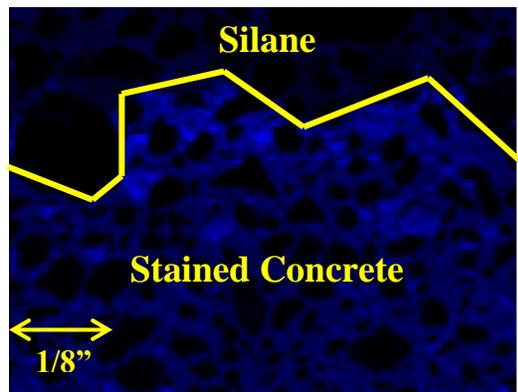
**Figure 4:** An example of a cluster map.

**Table 1:** Legend for the compositional map in Figure 4

Color	Type	Chemical Composition	Counts per Pixel
Red	High S Cement Paste	Calcium Sulfur Silicon	$\geq 11670$ $\geq 794$ $\geq 1028$
Green	Medium S Cement Paste	Calcium Sulfur Silicon	$\geq 11670$ $\geq 491$ $\geq 1028$
Blue	Low S Cement Paste	Calcium Sulfur Silicon	$\geq 11670$ $\geq 232$ $\geq 1028$
Cyan	Ca Rich Cement Paste with no S	Calcium	$\geq 11670$
Yellow	High Si Aggregate	Silicon	$\geq 9073$
Magenta	High K Aggregate	Potassium	$\geq 1976$

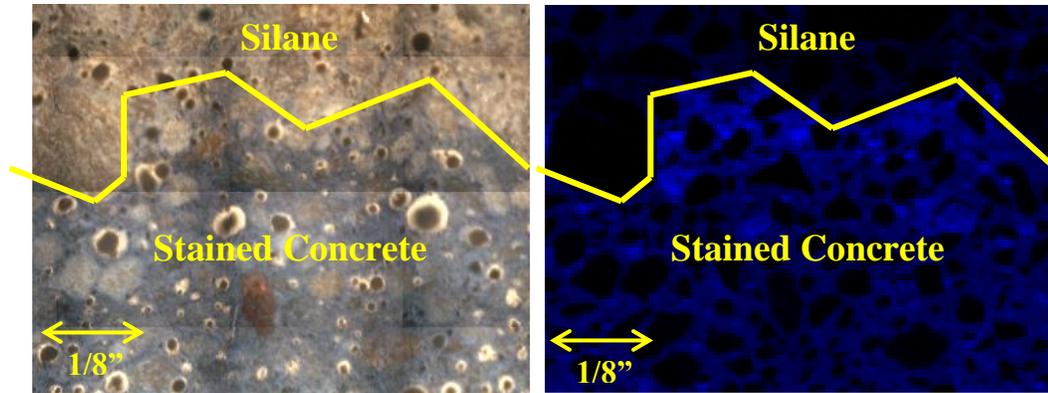
### 3.4 Using $\mu$ -XRF to Identify Silane in Concrete

To establish a method of detecting the silane layer in concrete, a series of scans were performed on both samples that contained silane and samples that did not contain silane. Samples from various bridges in Oklahoma that had been treated with silane were obtained and investigated. Data from the field samples containing silane that had been in service in bridges for 5-25 years were compared to samples that did not contain silane. The testing shows that  $\mu$ -XRF displays a few chemical clues that could help to identify the presence of silane. One of these clues, as shown in Figure 5, was a noticeable high band of sulfur (i.e. bright blue pixels) which was found just below the silane boundary.



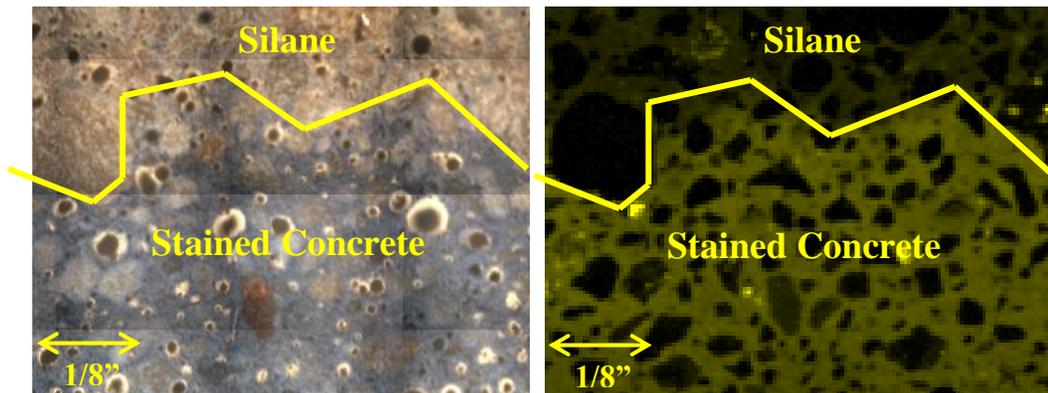
**Figure 5:** Example of a high band of sulfur found just below the silane boundary.

To confirm this observation, the sample was ponded in a chlorine based colored dye for 5 minutes and rescanned. The dye would permeate and stain the concrete only where silane was not present, thus establishing a visual contrast. A comparison of an optical image of the sample after it was ponded in colored dye and the sulfur image is shown in Figure 6. The silane boundary has been highlighted with a yellow line.



**Figure 6:** (Left) optical image with colored dye and (right) elemental sulfur image from the  $\mu$ -XRF.

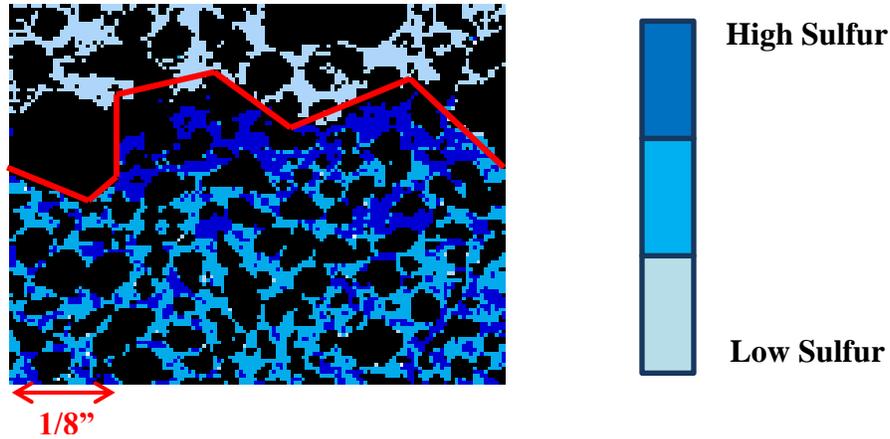
A similar observation was found in the chlorine image, where the area containing silane has a lower chlorine concentration than the area that does not contain silane, as shown in Figure 7.



**Figure 7:** (Left) optical image with colored dye and (right) elemental chlorine image from the  $\mu$ -XRF

By using these clues in conjunction with the cluster analysis technique, the aggregates were removed altogether and the cement paste was segmented based on varying sulfur concentrations, producing a cluster map like that shown in Figure 8. The high sulfur concentration band that was found just under the silane boundary in Figure 5 is represented by an area of dark blue in Figure 8. Following this same pattern, medium and low sulfur concentrations are represented by medium

and light blue, respectively. The cutoff points for each color were somewhat arbitrary, where each color indicates 1/3 of the total sulfur concentration range. Therefore the dark, medium, and light blue areas represent the highest third, intermediate third, and lowest third of the total sulfur concentration range, respectively. The same silane boundary that was found in Figures 5 and 6 has been highlighted by a red line in Figure 8.

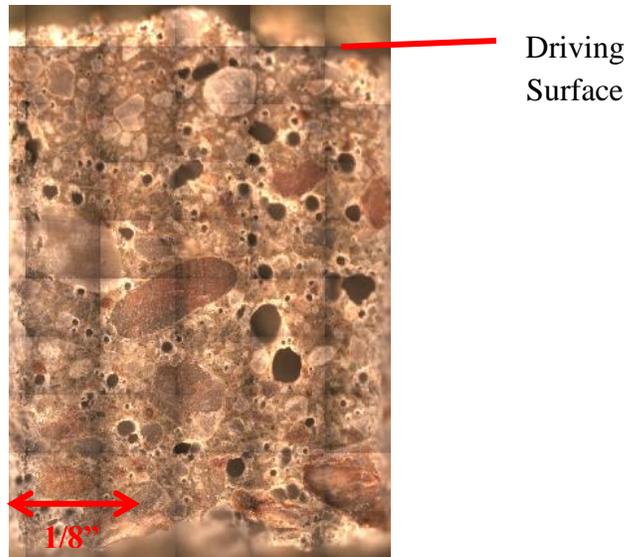


**Figure 8:** Example of a segmented cement paste cluster map based on varying sulfur concentrations.

These observations demonstrate the  $\mu$ -XRF's ability to provide chemical clues that can be used in conjunction with other techniques to help better understand and identify the presence of silane in concrete.

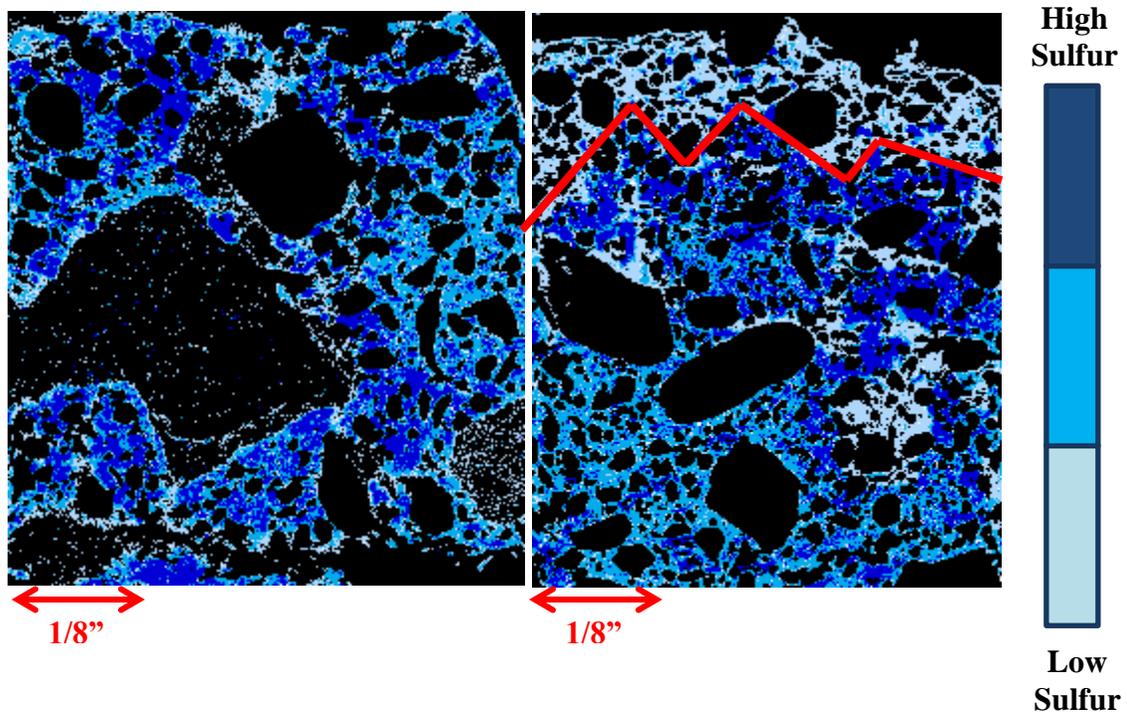
### 3.5 Field Cores

A total of 12 core samples of approximately 0.5" in diameter x 1" in height that were taken from various bridges in the state of Oklahoma were investigated using  $\mu$ -XRF to help determine whether or not silane existed on the driving surface of the bridge deck. Each core sample was polished through the depth to establish a flat surface, as shown in Figure 9, and then scanned using  $\mu$ -XRF.



**Figure 9:** Example of a core sample that has been polished through the depth.

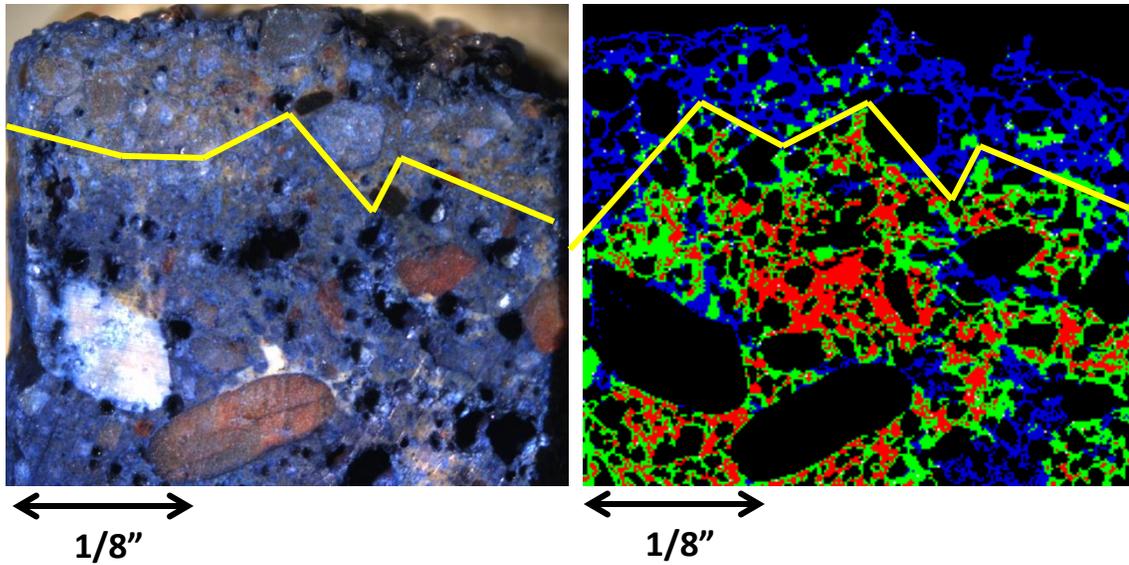
Based on the chemical clues described in the previous section, a total of 10 samples showed no definitive evidence of the presence of silane according to the observation made in the sulfur image. As shown on the left in Figure 10, those that showed no signs of silane were deemed so by an absence of the high sulfur band and displayed no particular sulfur pattern. Using this same observation, a total of 2 samples showed definitive evidence of the presence of silane, as shown by the example on the right in Figure 10.



**Figure 10:** (Left) cement paste cluster map with no band of sulfur (right) cement paste cluster map with a band of sulfur. The sulfur band has been shown to correspond to the presence of silane.

### 3.6 Chlorine Based Dyed

In addition to  $\mu$ -XRF, a second technique of using a chlorine based dye was employed to determine the presence of silane. Each core was ponded in the dye for 5 minutes and rescanned with  $\mu$ -XRF. As discussed in Section 3.4, the dye would permeate and stain the concrete only where silane was not present, thus establishing a visual contrast that could be seen with the naked eye; while simultaneously establishing a greater chemical contrast by supplying additional chlorides that diffuse into the untreated area. A comparison of the visual contrast and the chemical contrast is shown in Figure 11.



**Figure 11:** (Left) optical image of a core after ponding in chlorine based dye (right) chlorine based cement paste cluster map.

### 3.7 Results

The chemical clues provided by  $\mu$ -XRF as well as the chlorine based colored dye were used to determine the presence of silane in all field core samples. Table 2 is a summary of the results of each technique used on each sample to determine the presence of silane.

**Table 2:** Summary of results from each technique used to determine the presence of silane in field cores

Specimen:	Years of Service	Location:	Results from Each Technique			Does Sample Contain Silane?
			Sulfur Image:	Chlorine Image:	Cl Based Dye	
I-40 #1	27	Shoulder	Yes (0.12in)	Yes (0.12in)	Yes (0.13in)	Yes
I-40 #2	27	Travel Lane	Yes (0.13in)	Yes (0.13in)	No	No
SH-99 #1	22	Travel Lane	No	No	No	No
SH-99 #2	22	Shoulder	No	No	No	No
SH-99 #3	22	Shoulder	No	No	No	No

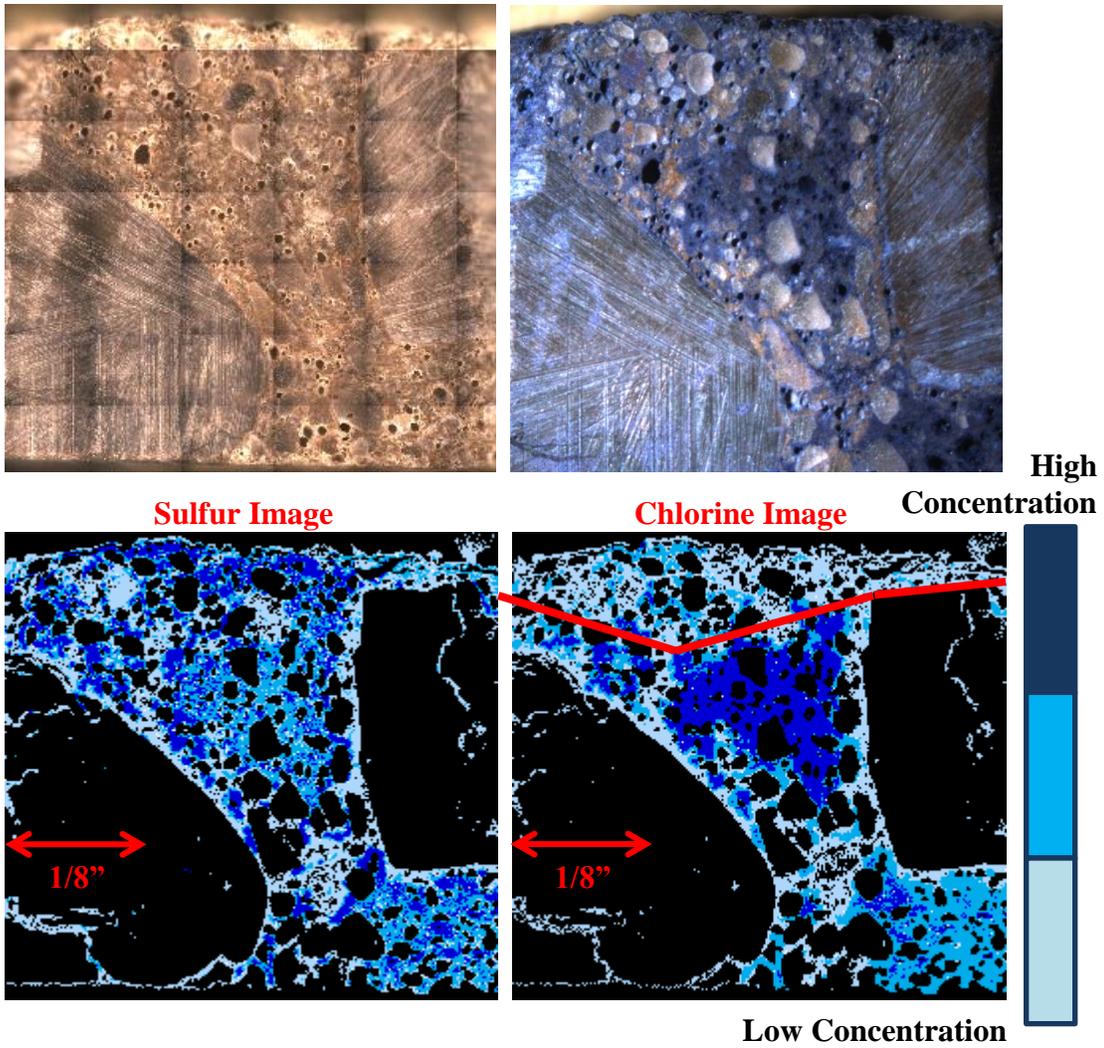
SH-99 #4	22	Travel Lane	No	No	No	No
US-62 #1	17	Shoulder	No	No	Yes (0.06in)	Yes
US-62 #2	17	Travel Lane	No	Yes (0.17in)	No	No
SH-3 #1	12	Shoulder	No	No	No	No
SH-3 #2	12	Travel Lane	No	Yes (0.08in)	No	No
SH-51 #1	7	Shoulder	No	No	No	No
SH-51 #2	7	Travel Lane	No	No	No	No

During additional testing to confirm the ability of using  $\mu$ -XRF to determine the presence of silane by means of using the sulfur and chlorine images, it was found that the two images did not always agree with one another nor did they consistently agree with the chlorine based dye technique. Although  $\mu$ -XRF can offer clues to help understand and identify the presence of silane, further research should be done before this technique can be used to identify silane on its own.

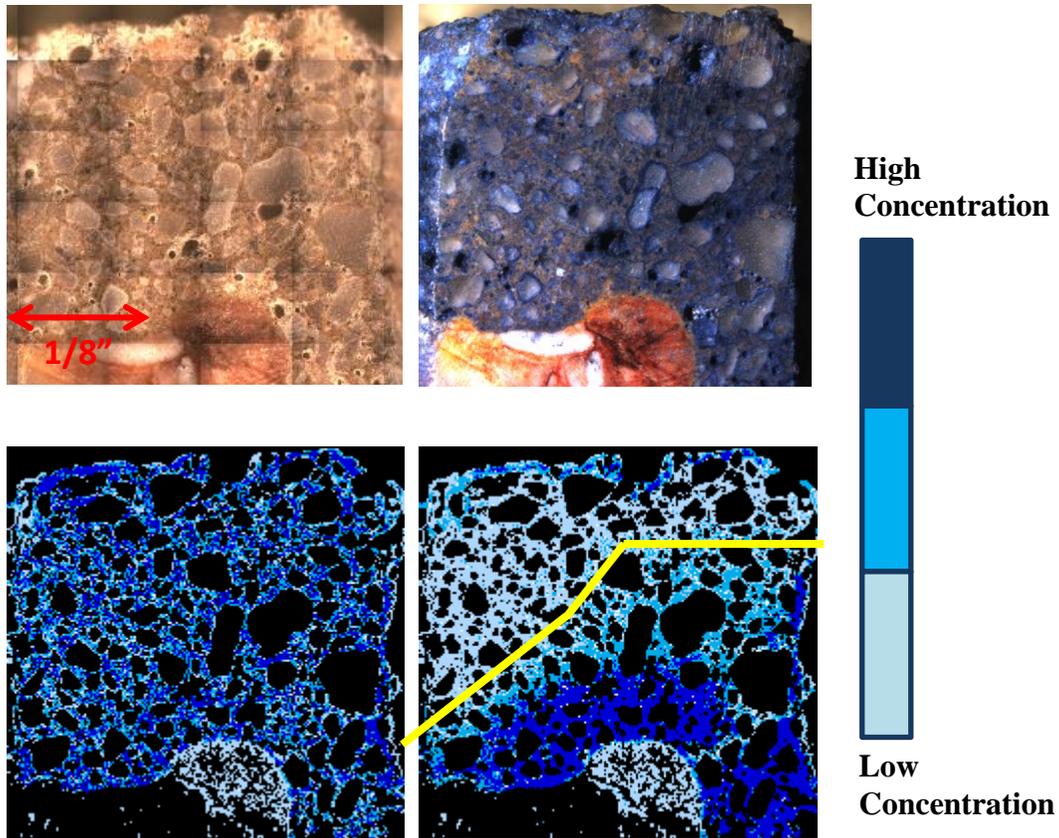
The chlorine based dye on the other hand was a very simple and effective method to determine the presence of silane on concrete core samples. Due to the uncertainty of using the sulfur and chlorine images, the use of the chlorine-based dye was ultimately used to determine the presence of silane.

### 3.8 Additional Observations

The determination of the presence of silane using the sulfur image and the chlorine image are in agreement on all samples except two: SH3 #2 and US62 #2. While the sulfur image suggests that there is no evidence of silane, the chlorine image suggests that there is. The sulfur and chlorine based cement paste maps for SH3 #2 and US62 #2 are compared in Figures 12 and 13, respectively, where the suggested silane boundary in the chlorine image is highlighted by a red line.



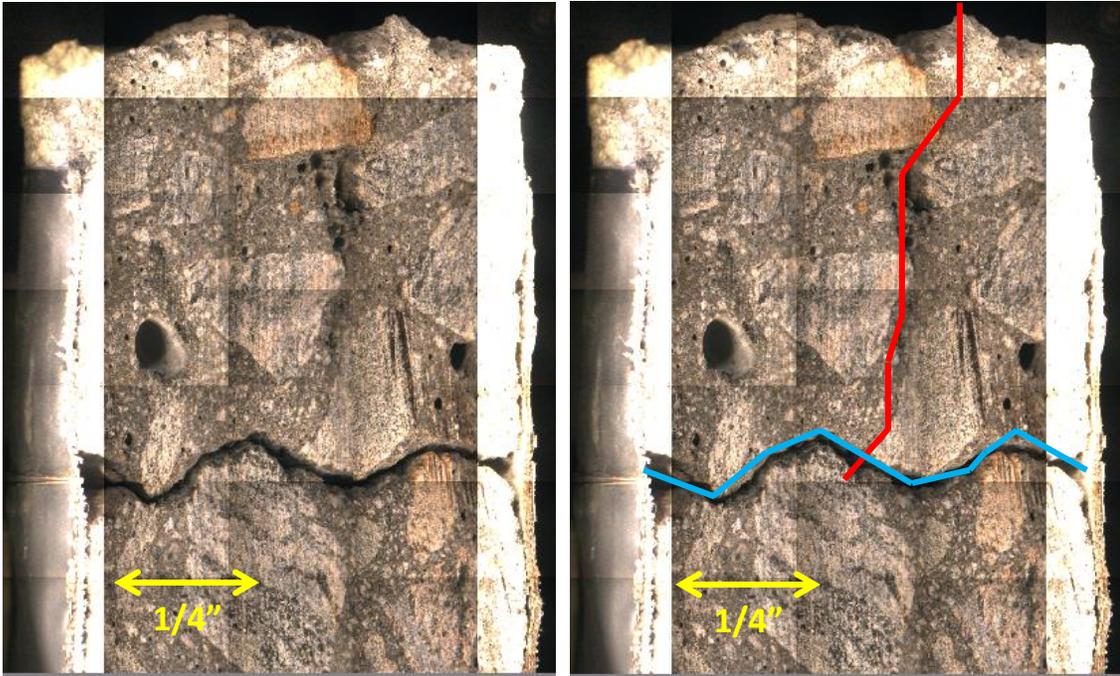
**Figure 12:** SH3 #2 sample (top left) non-dyed optical image (top right) optical image of dyed sample (bottom left) segmented sulfur image (bottom right) segmented chlorine image.



**Figure 13:** US62 #2 sample (top left) non-dyed optical image (top right) optical image of dyed sample (bottom left) segmented sulfur image (bottom right) segmented chlorine image.

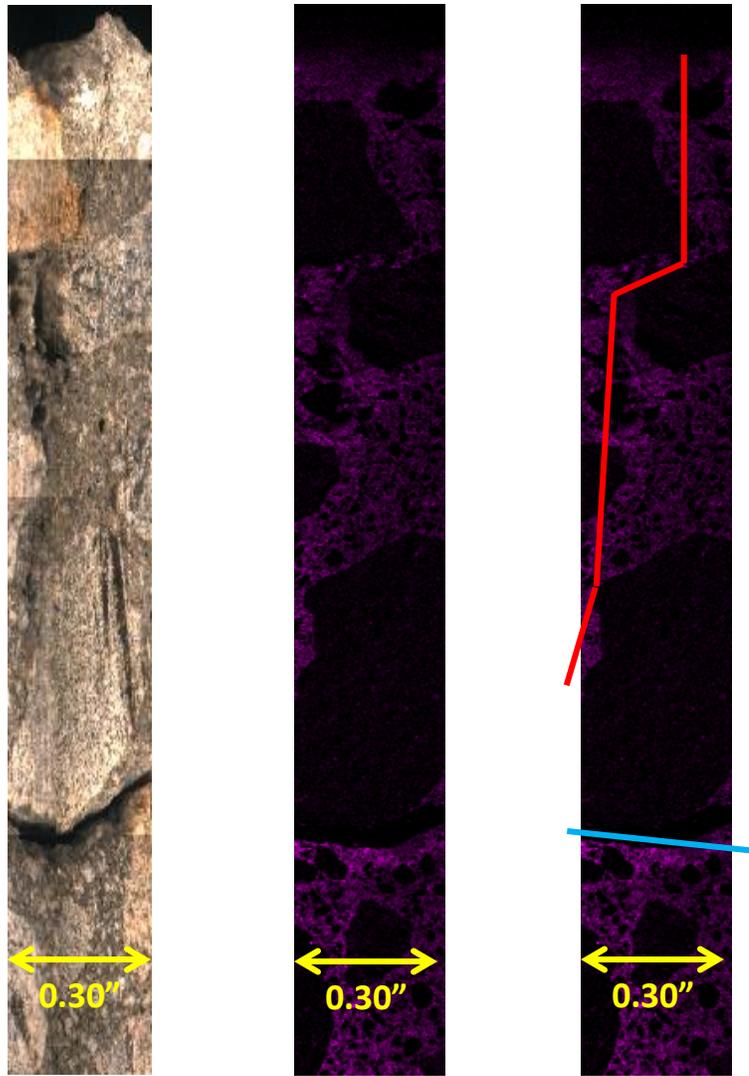
Since chlorides are not a part of the production of cement or concrete, further investigation was needed to help explain why a higher concentration of chlorides exists below the silane boundary.

This higher concentration of chlorides just below the silane boundary could be due to a crack that has propagated through the layer that has been previously treated with silane. As shown in Figure 14, a crack provides a direct pathway for chlorides to diffuse deeper into the concrete.



**Figure 14:** Concrete core sample. (Left) optical image (right) cracks highlighted in optical image.

As shown in Figure 15, a crack allows chlorides to penetrate deeper into the sample as well as diffuse perpendicularly to the cracks. Although the portion of concrete that has been treated with silane may be protected from chloride ingress, cracks can allow chlorides and other deleterious materials to bypass this protective layer. For more information on surface treatments, including silane, siloxane, and how cracks affect the treatment's performance see ACI 515, ACI 546, and Kosmatka (1997).



**Figure 15:** Concrete core sample. (Left) optical image (middle) chlorine image (right) cracks highlighted in chlorine image.

## CHAPTER IV

### USING NON-DESTRUCTIVE FIELD TESTING TECHNIQUES TO DETECT THE PRESENCE OF SILANE IN CONCRETE

#### **4.1 Overview**

A field investigation was conducted that served two purposes. First, core samples were taken from various bridges in the state of Oklahoma to be tested in the laboratory. The purpose of this testing was to determine the service life of silane treatments. Also, a field test was used to investigate the presence of the silane treatment.

#### **4.2 Core Samples**

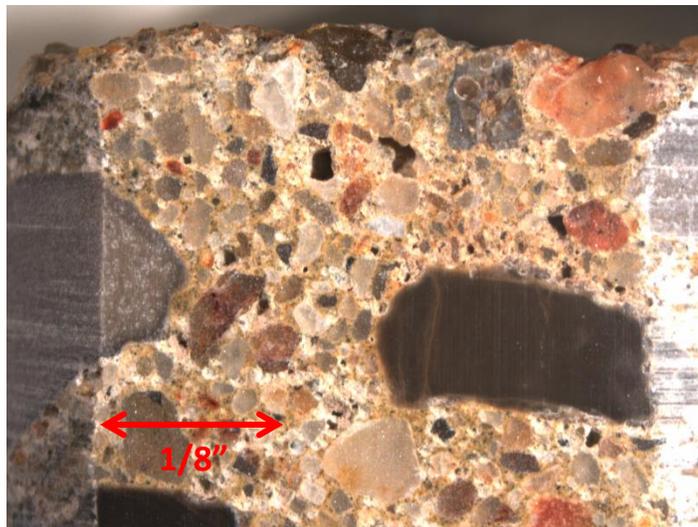
In order to determine the service life of silane treatments, cores were taken from bridges in the state of Oklahoma, where the treatments had an age range of 5-10 years. Cores were collected for further testing in the laboratory by means of various dyes.

Before cores could be taken, an area on the shoulder was swept clean of loose debris. Cores, which were approximately 1/2" diameter x 3/4" high, were taken using a drill bit and cordless drill as shown in Figure 16. Whenever possible, cores were also taken from the travel lane in order to examine the effects of erosion on the silane treatment.



**Figure 16:** (Left) taking cores with a cordless drill (right) example of cores taken.

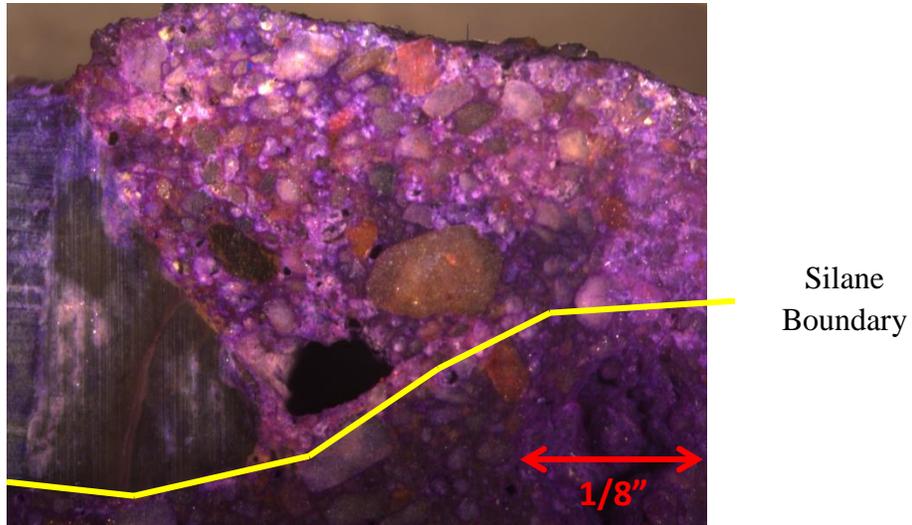
After collecting core samples, each core was polished on its side to establish a flat surface as shown in Figure 17.



**Figure 17:** Example of core sample that has been polished.

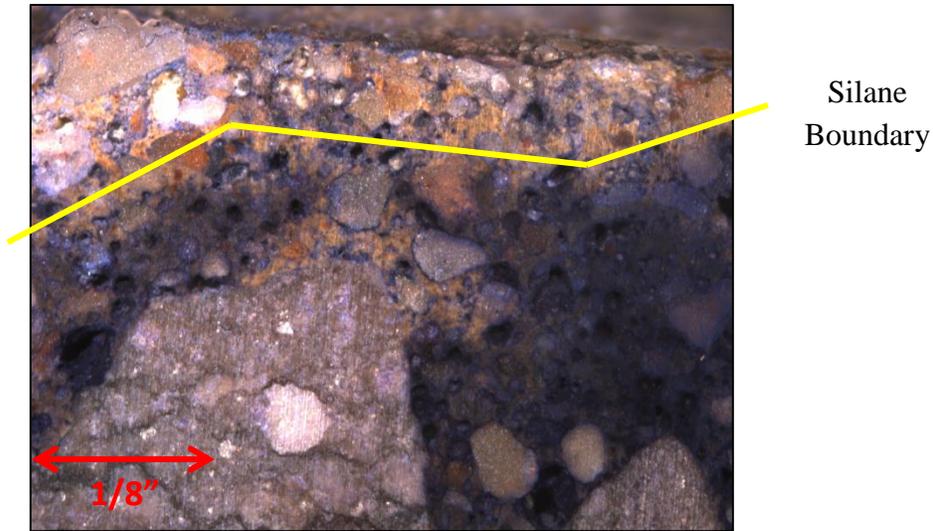
Once the core was polished, the core was ponded in brominated-blue dye for 30 seconds that would stain the area of concrete that does not contain silane blue as shown in Figure 18. In

addition to a visual contrast, the brominated dye established an observable chemical contrast by attaching a bromine marker to the silane molecules.



**Figure 18:** Example of a core that was polished in brominated-blue dye

After ponding in brominated-blue dye, the core was polished to expose a fresh surface and then ponded in a chlorine based dye for 30 minutes, which also stains the area of concrete that does not contain silane blue as shown in Figure 19. In addition to a visual contrast, the chlorine based dye established an observable chemical contrast by increasing the chlorine concentration in the area of concrete that does not contain silane.



**Figure 19:** Example of a core that was ponded in a chloride-based dye.

By using the brominated and chlorine-based dyes, the presence of silane was determined for cores taken from 24 different bridges. The depth of the silane boundary, like that shown in Figure 19, was determined.

### 4.3 Wenner Probe

#### 4.3.1 Overview

Among the field testing techniques employed was the 4-point Wenner Probe, which measures the apparent resistance of concrete. The resistance of the bridge deck was monitored over time using the Wenner probe by ponding the surface of the bridge deck with water and taking measurements at specified time intervals. As determined by laboratory tests performed before all field testing, concrete that has been treated with silane has 3 to 8 times higher resistance than concrete with no treatment. A high resistance, as well as increasing resistance over time, suggests evidence of the presence of silane treatments.

## 4.3.2 Laboratory Testing

### 4.3.2.1 Methodology

Before taking the Wenner Probe out into the field, a small study was conducted in the laboratory to determine if concrete that had been treated with silane had a different resistance than concrete that had not been treated. The resistivity of the concrete was monitored over time where water was allowed to permeate through the matrix for 0, 30, 60, 90, and 120 minutes.

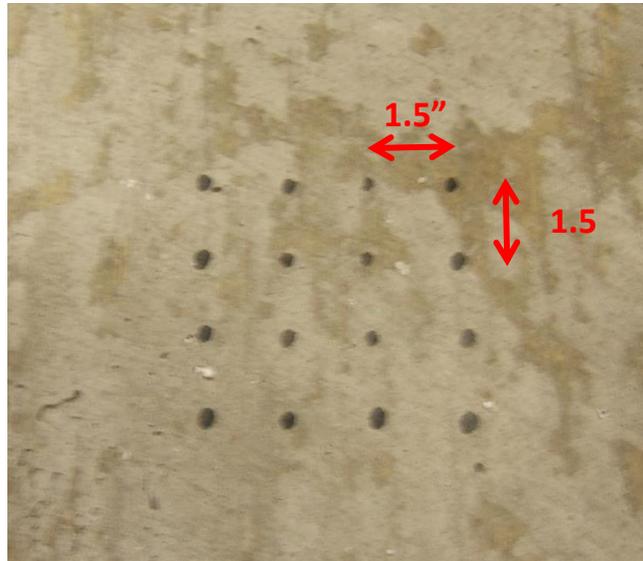
As shown in Figure 20, two 12" x 12" x 2" specimens were cast and allowed to cure for about a week before testing.



**Figure 20:** Example of (left) specimen mold and (right) a 12" x 12" x 2" specimen.

One specimen was treated with silane, while the second remained untreated during testing. The silane used is SIL-ACT ATS-42 from Advanced Chemical Technologies. A brush was used to apply the silane treatment to the top (i.e. finished) surface and allowed to cure at room temperature for 5 minutes. The specimen was then turned over and treatment was applied in the same manner to the bottom (i.e. formed) surface as well as the sides of the specimen and allowed to cure at room temperature for 5 minutes. This process was repeated until each face had received a total of 3 treatments.

Next a grid was placed on the formed surface of both specimens, as shown in Figure 21, to mark where measurements would be taken with the Wenner probe.



**Figure 21:** Example of a grid placed on the formed side of a specimen.

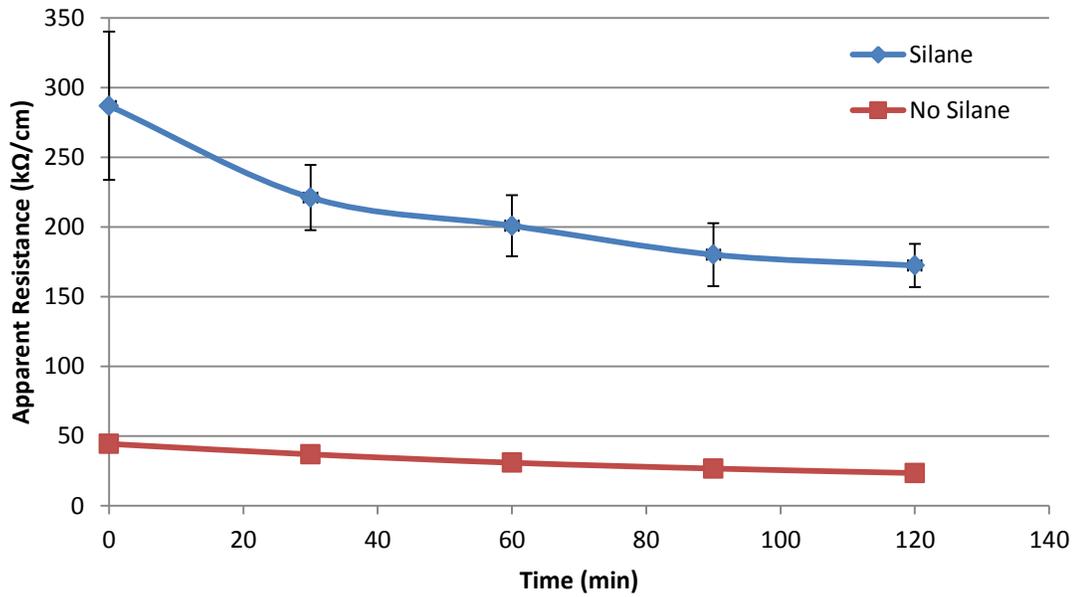
With the grid placed, the formed surface of both specimens was dampened in order to take preliminary measurements (i.e. resistance at 0 minutes of ponding). Next, as shown in Figure 22, columns were placed on top of the formed side and putty was placed around the base of the column to create a water tight seal. Then each column was filled with water and allowed to pond for 30 minutes. After 30 minutes, the columns were removed and measurements were taken from both specimens. The columns were then placed back and the process was repeated until measurements were taken at 30, 60, 90, and 120 minutes of ponding.



**Figure 22:** Example of (left) water column setup and (right) creating a water tight seal.

#### 4.3.2.2 Results

After all measurements were taken, the average resistance vs. time was plotted for each specimen and compared, as shown in Figure 23. By comparing the results in Figure 23, it is clear that concrete that has been treated with silane has a resistance that is much higher than that of concrete that has not been treated with silane. The presence of silane on bridge decks were then determined using this observation.



**Figure 23:** Comparison of average resistance vs. time between specimens treated with silane and specimens not treated with silane.

#### 4.3.3 Field Testing

Before using the Wenner probe, the area chosen for testing had to be prepared by sweeping away loose debris and placing four grids on the bridge deck from which measurements would be taken, as shown in Figure 24. The spacing between the points in the grid was 1.5” in each direction to match the spacing of the contact points of the Wenner probe.



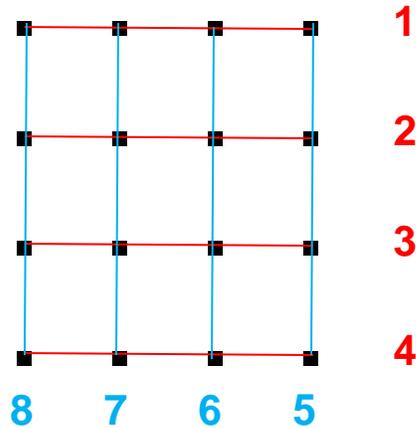
**Figure 24:** Preparing the test area by (left) sweeping away loose debris and (right) placing grids on the bridge deck.

Next, preliminary readings (i.e. zero minutes of ponding) were taken by dampening the surface where each grid was located as shown in Figure 25, waiting 30 seconds to allow the water to soak in and the resistance to reach a steady state, then taking measurements using the Wenner probe. The four contact points on the Wenner probe must be moist in order to take measurements, hence the need to dampen the surface before taking preliminary measurements.



**Figure 25:** Example of dampening the surface before taking preliminary readings.

A total of 8 measurements were taken each time from each grid as shown in Figure 26.



**Figure 26:** Example of taking measurements.

After taking measurements from each grid, the process was repeated. This time a cup of water was poured on top of each grid and allowed to pond for 60 seconds, as shown in Figure 27.

Measurements were taken in the same manner described in Figure 26.



**Figure 27:** Example of (left) cup of water and (right) ponding for 60 seconds.

After the second set of measurements, water columns were set on top of each grid as shown in Figure 28. Putty was used to form a water tight seal at the bottom of each column and weights

were placed on top of the columns to insure a better seal as shown in Figure 29. Next, the columns were filled with water past the seal and allowed to pond for 30 minutes.



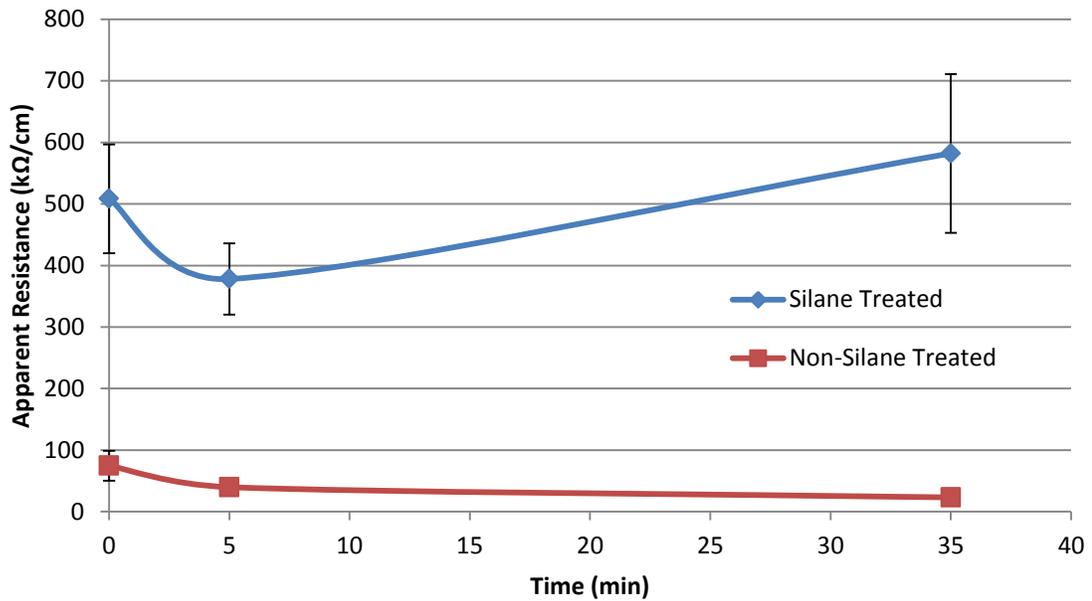
**Figure 28:** Example of a water column setup.



**Figure 29:** Example of using weights to insure a better seal.

Once the ponding was completed, measurements of each grid were taken in the manner described in Figure 26.

As shown by the example in Figure 30, all measurements were plotted and compared. Figure 30 shows a comparison between a bridge deck that does show evidence of the presence of silane (SH-18 #1 Grid #3) and a bridge deck that does not (US-75 #1 Grid #1).



**Figure 30:** Example of a comparison between a bridge deck that shows evidence of silane (SH-18 #1 Grid #3) and a bridge that does not (US-75 Grid #1).

#### 4.4 Conclusion

The data from these field techniques were then compared with laboratory techniques in order to determine the presence and effectiveness of silane treatments. This comparison is described in detail in Chapter 5.

## CHAPTER V

### COMPARISON OF NON-DESTRUCTIVE LABORATORY AND FIELD TESTING TECHNIQUES

#### **5.1 Overview**

Various field and laboratory techniques were employed to investigate the presence and effectiveness of silane in concrete from several bridge decks in the state of Oklahoma. Among these techniques were the 4-Point Wenner Probe, a brominated dye, a chlorine based dye, and Micro X-ray Fluorescence ( $\mu$ -XRF). The Wenner Probe was used on the shoulder lane of each bridge location for a ponding time of 30 minutes. Sample cores (approximately 0.5" in diameter x 1" in height) were taken from each bridge deck and tested using the brominated dye, chlorine based dye, and  $\mu$ -XRF. Ponding times for the brominated and chlorine based dyes were 30 seconds and 30 minutes, respectively.

#### **5.2 Results**

Table 3 summarizes the results of the determination of the presence of silane using all three techniques. Table 4 summarizes the results of the technique that was considered to be the best at determining the presence of silane as well as provides an estimate of the depth of penetration of the silane treatment.

**Table 3:** Summary of results from all techniques used.

Facility	Latitude Longitude	Years of Service	Sample Location	Does Technique Show Silane?				
				Wenner Probe	Bromin -ated Dye	Cl- Based Dye	Sulfur Image ( $\mu$ -XRF)	Chlorine Image ( $\mu$ -XRF)
SH18	35° 39' 02.4"	6	Shoulder	Y	N	N	-	-
	-96° 53' 17.1"		Travel Lane	-	***	***	-	-
SH18	35° 38' 52.2"	6	Shoulder	Y	N	Y	-	-
	-96° 53' 16.2"		Travel Lane	-	N	Y	-	-
SH33	35° 57' 57.5"	7	Shoulder	Y	**	**	-	-
	-97° 14' 02.4"		Travel Lane	-	**	**	-	-
SH33	35° 52' 16.5"	6	Shoulder	Y	N	Y	-	-
	-97° 36' 48.5"		Travel Lane	-	N	Y	-	-
SH33	35° 52' 16.5"	6	Shoulder	Y	N	N	-	-
	-97° 36' 21.6"		Travel Lane	-	**	**	-	-
SH33	35° 59' 18.6"	10	Shoulder	Y	N	Y	-	-
	-96° 17' 07.4"		Travel Lane	-	N	Y	-	-
SH33	35° 57' 05.9"	9	Shoulder	Y	N	Y	-	-
	-97° 16' 09.0"		Travel Lane	-	N	N	-	-
SH33	35° 57' 07.1"	9	Shoulder	Y	Y	N	-	-
	-97° 16' 09.1"		Travel Lane	-	N	N	-	-
SH51	36° 06' 57.0"	5	Shoulder	N	N	Y	Y	Y
	-97° 06' 08.0"		Travel Lane	-	N	Y	-	-

SH51	36° 06' 56.8"	5	Shoulder	Y	N	N	N	N
	-97° 05' 57.0"		Travel Lane	-	N	Y	-	-
SH51	36° 07' 39.1"	Not Treated	Shoulder	Y	N	N	-	-
	-97° 04' 09.1"		Travel Lane	-	**	**	-	-
SH51	36° 06' 96.0"	Not Treated	Shoulder	Y	N	N	-	-
	-97° 00' 46.5"		Travel Lane	-	**	**	-	-
SH51	36° 06' 98.8"	8	Shoulder	Y	Y	Y	-	-
	-96° 56' 72.0"		Travel Lane	-	**	**	-	-
US75	35° 51' 59.0"	8	Shoulder	N	N	N	-	-
	-96° 03' 43.8"		Travel Lane	-	Y	Y	-	-
US75	35° 57' 22.0"	5	Shoulder	Y	Y	Y	-	-
	-96° 04' 19.2"		Travel Lane	-	N	Y	-	-
US377 / SH99	35° 34' 32.7"	6	Shoulder	Y	N	Y	-	-
	-96° 39' 49.8"		Travel Lane	-	N	***	-	-
US377 / SH99	35° 34' 31.8"	6	Shoulder	Y	N	Y	-	-
	-96° 39' 48.6"		Travel Lane	-	N	Y	-	-
US377 / SH99	35° 41' 06.3"	6	Shoulder	Y	N	N	-	-
	-96° 39' 45.4"		Travel Lane	-	N	Y	-	-
US377 / SH99	35° 41' 22.9"	6	Shoulder	Y	N	Y	-	-
	-96° 39' 45.1"		Travel Lane	-	N	Y	-	-

**\*\*No sample taken.**

**\*\*\*An issue occurred with the sample (e.g. the sample broke during preparation) and the test was unable to be performed.**

**N = sample displayed the possibility of a silane layer, but the evidence was not definitive.**

**Table 4:** Determining the presence and approximate depth of penetration of silane using the chlorine-based dye technique.

Facility	Latitude Longitude	Years of Service	Sample Location	Does Sample Have Silane?	
				Cl-Based Dye	Depth (in)
SH18	35° 39' 02.4" -96° 53' 17.1"	6	Shoulder	N	-
			Travel Lane	***	-
SH18	35° 38' 52.2" -96° 53' 16.2"	6	Shoulder	Y	1/8
			Travel Lane	Y	1/8
SH33	35° 57' 57.5" -97° 14' 02.4"	7	Shoulder	**	-
			Travel Lane	**	-
SH33	35° 52' 16.5" -97° 36' 48.5"	6	Shoulder	Y	1/8
			Travel Lane	Y	1/16
SH33	35° 52' 16.5" -97° 36' 21.6"	6	Shoulder	N	-
			Travel Lane	**	-
SH33	35° 59' 18.6" -96° 17' 07.4"	10	Shoulder	Y	1/8
			Travel Lane	Y	¼
SH33	35° 57' 05.9" -97° 16' 09.0"	9	Shoulder	Y	1/8
			Travel Lane	N	-
SH33	35° 57' 07.1" -97° 16' 09.1"	9	Shoulder	N	-
			Travel Lane	N	-
SH51	36° 06' 57.0" -97° 06' 08.0"	5	Shoulder	Y	1/8
			Travel Lane	Y	1/16
SH51	36° 06' 56.8" -97° 05' 57.0"	5	Shoulder	Y	1/16
			Travel Lane	Y	1/16
SH51	36° 07' 39.1" -97° 04' 09.1"	Not Treated	Shoulder	N	-
			Travel Lane	**	-
SH51	36° 06' 96.0"	Not Treated	Shoulder	N	-

	-97° 00' 46.5"		Travel Lane	**	-
SH51	36° 06' 98.8"	8	Shoulder	Y	1/8
	-96° 56' 72.0"		Travel Lane	**	-
US75	35° 51' 59.0"	8	Shoulder	N	-
	-96° 03' 43.8"		Travel Lane	Y	1/4
US75	35° 57' 22.0"	5	Shoulder	Y	1/16
	-96° 04' 19.2"		Travel Lane	Y	3/16
US377 / SH99	35° 34' 32.7"	6	Shoulder	Y	3/16
	-96° 39' 49.8"		Travel Lane	***	-
US377 / SH99	35° 34' 31.8"	6	Shoulder	Y	1/8
	-96° 39' 48.6"		Travel Lane	Y	1/16
US377 / SH99	35° 41' 06.3"	6	Shoulder	N	-
	-96° 39' 45.4"		Travel Lane	Y	1/8
US377 / SH99	35° 41' 22.9"	6	Shoulder	Y	3/16
	-96° 39' 45.1"		Travel Lane	Y	1/8

**\*\*No sample taken.**

**\*\*\*An issue occurred with the sample (e.g. the sample broke during preparation) and the test was unable to be performed.**

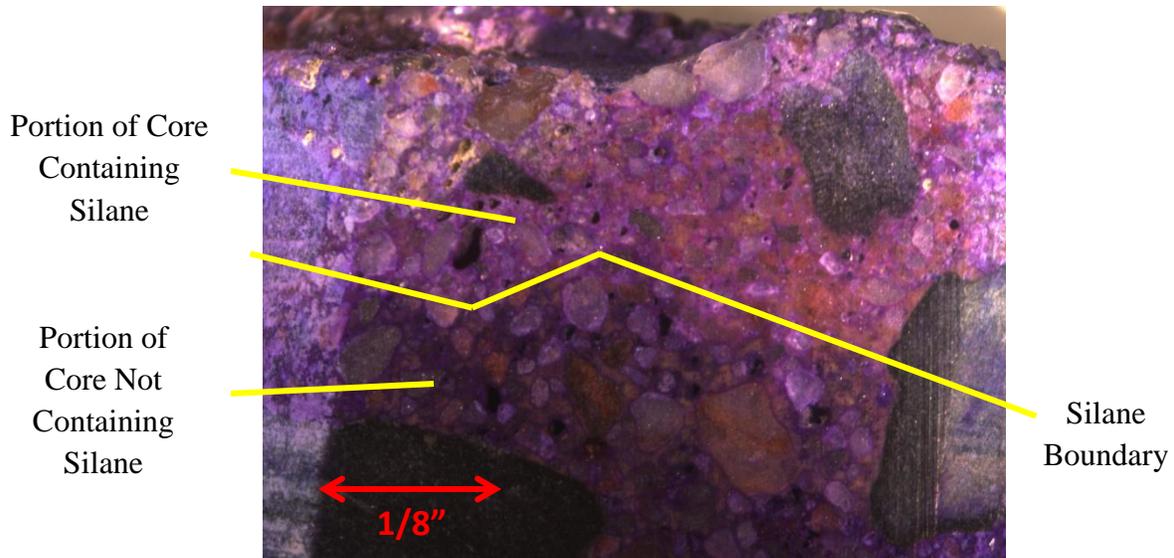
**N = sample displayed the possibility of a silane layer, but the evidence was not definitive.**

### 5.3 Conclusions

Two of the bridge decks on SH-51 were reported by the Oklahoma Department of Transportation (ODOT) to have never been treated with silane. Despite this information, the Four-Point Wenner Probe suggests that a silane treatment exists on the bridge deck. For this reason, it suggested that the use of this technique to determine the presence of silane in the field needs further development.

By observing the core samples after being ponded in brominated dye, it was concluded that the brominated dye also needs further development for determining the presence of silane. When

comparing the brominated and chlorine-based dyes, the brominated dye almost never suggests the presence of silane. Of those that do suggest the presence of silane, it was noticed that the brominated dye was effective enough to stain the silane treated portion as well as the non-treated portion. The portion of the core sample that did not contain silane stained a darker shade of blue than the portion containing silane, as shown in Figure 31.



**Figure 31:** Example of brominated dye staining both portions of the concrete sample.

Since the Wenner Probe and the brominated dyes posed these issues and the  $\mu$ -XRF technique agreed with the chlorine-based dye, it was concluded that the chlorine-based dye was the best method to use to determine the presence of silane.

The next step was to determine the useful lifespan of the silane treatment on a concrete bridge deck using the data from the chlorine-based dye method. Table 5 summarizes this data.

**Table 5:** Summary of data from chlorine-based dye.

<b>Years of Service</b>		5	6	7	8	9	10
<b>Total Cores Tested</b>		6	13	2	3	8	4
<b>Travel Lane</b>	<b>Silane</b>	3	5	0	1	2	2
	<b>No Silane</b>	0	0	1	0	2	0
<b>Shoulder</b>	<b>Silane</b>	2	5	0	2	1	1
	<b>No Silane</b>	1	3	1	0	3	1

As shown in Table 6, the useful lifespan of silane on concrete bridge decks in the state of Oklahoma is summarized.

**Table 6:** Summary of useful lifespan of silane treatment.

<b>Has Silane</b>	Year 5-6	Year 9-10
<b>Travel Lane</b>	100%	66.7%
<b>Shoulder</b>	63.6%	33.3%

#### **5.4 Discussion and Recommendations**

From Table 6, it was concluded that the useful lifespan of a silane treatment on a concrete bridge deck is 5-6 years. Table 5 also shows that the shoulder lane of the bridge deck consistently has more cases where silane is not found. This could be due to an uneven application of the silane treatment on the entire bridge deck, or that the shoulder did not get the same coverage during the silane application. This information data suggests that the silane seems to be effective at least through six years of service. There does appear to be a reduction in the effectiveness of silane after being in service after nine years of service of about 30% of the bridges. Because only a few samples were investigated between these periods it is difficult to comment on the exact loss in effectiveness of the silane. It is recommended that silane either be reapplied or no longer expected to resist outside chemicals after 9 years of service.

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