

EXPECTED LIFE OF SILANE WATER REPELLANT TREATMENTS ON BRIDGE DECKS

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16. ABSTRACT This report covers techniques used to evaluate the presence of silane coatings on bridge decks in the lab and in the field. After these techniques are established they are then used to determine the effective service life of silane and the ability to reapply silane to the surface of the concrete. The following techniques are investigated in this study: surface resistivity, German water permeability, contact angle measurements, selective dyes, and a XRF Microscope. The most promising techniques were used to evaluate the field performance that had been in service between 5 and 28 years. The work showed that the silane coatings lasted at least 6 years and that after 9 years about 30% of the silane coatings were no longer effective. Lab based reapplication efforts suggest that it is possible to reapply silane; however, additional efforts are needed above what is typically done for concrete less than a year old.			
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SI* (MODERN METRIC) CONVERSION FACTORS

APPROXIMATE CONVERSIONS TO SI UNITS				
SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
LENGTH				
in	Inches	25.4	Millimeters	Mm
ft	Feet	0.305	Meters	M
yd	Yards	0.914	Meters	M
mi	Miles	1.61	Kilometers	Km
AREA				
in²	square inches	645.2	square millimeters	mm ²
ft²	square feet	0.093	square meters	m ²
yd²	square yard	0.836	square meters	m ²
ac	Acres	0.405	Hectares	Ha
mi²	square miles	2.59	square kilometers	km ²
VOLUME				
fl oz	fluid ounces	29.57	Milliliters	mL
gal	Gallons	3.785	Liters	L
ft³	cubic feet	0.028	cubic meters	m ³
yd³	cubic yards	0.765	cubic meters	m ³
NOTE: volumes greater than 1000 L shall be shown in m ³				
MASS				
oz	Ounces	28.35	Grams	G
lb	Pounds	0.454	Kilograms	kg
T	short tons (2000 lb)	0.907	megagrams (or "metric ton")	Mg (or "t")
TEMPERATURE (exact degrees)				
°F	Fahrenheit	5 (F-32)/9 or (F-32)/1.8	Celsius	°C
ILLUMINATION				
fc	foot-candles	10.76	Lux	lx
fl	foot-Lamberts	3.426	candela/m ²	cd/m ²
FORCE and PRESSURE or STRESS				
lbf	Poundforce	4.45	Newtons	N
lbf/in²	poundforce per square inch	6.89	Kilopascals	kPa

APPROXIMATE CONVERSIONS FROM SI UNITS				
SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
LENGTH				
mm	Millimeters	0.039	inches	in
m	Meters	3.28	feet	ft
m	Meters	1.09	yards	yd
km	Kilometers	0.621	miles	mi
AREA				
mm ²	square millimeters	0.0016	square inches	in ²
m ²	square meters	10.764	square feet	ft ²
m ²	square meters	1.195	square yards	yd ²
ha	Hectares	2.47	acres	ac
km ²	square kilometers	0.386	square miles	mi ²
VOLUME				
mL	Milliliters	0.034	fluid ounces	fl oz
L	Liters	0.264	gallons	gal
m ³	cubic meters	35.314	cubic feet	ft ³
m ³	cubic meters	1.307	cubic yards	yd ³
MASS				
g	Grams	0.035	ounces	Oz
kg	Kilograms	2.202	pounds	Lb
Mg (or "t")	megagrams (or "metric ton")	1.103	short tons (2000 lb)	T
TEMPERATURE (exact degrees)				
°C	Celsius	1.8C+32	Fahrenheit	°F
ILLUMINATION				
lx	Lux	0.0929	foot-candles	Fc
cd/m ²	candela/m ²	0.2919	foot-Lamberts	Fl
FORCE and PRESSURE or STRESS				
N	Newtons	0.225	poundforce	Lbf
kPa	Kilopascals	0.145	poundforce per square inch	lbf/in ²

SI is the symbol for the International System of Units. Appropriate rounding should be made to comply with Section 4 of ASTM E380. (Revised March 2003)

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- Walt Peters
- Bryan Hurst
- Kenny Seward

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Chapter 1 - 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 lifespan of a silane coating or the ability to reapply this material. These areas will be discussed in this work.

In this report the research team will complete the following work. Each bullet item will also be a chapter in the report.

- Literature review of silane performance in concrete
- Establish laboratory techniques to find the presence of silanes in concrete
- Establish non-destructive field testing techniques to find the presence of silane
- Investigate field concrete for the presence of silane with these techniques
- Recommend a period for silane re-application
- Determine the ability to reapply silane in field concrete

This work will establish some important laboratory and field techniques that can be used to determine the presence and effectiveness of silane. This work will also provide important guidance to ODOT on the period of reapplication. These findings will be of great use to ODOT and other DOTs and will help extend the service life of the bridges in the state.

Chapter 2: Literature Review

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 fillers.

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].

2.1.1 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, alkoxy silanes 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 3: Using Laboratory Techniques to Find the Presence of Silanes in Concrete

3.1 Introduction

The focus of this chapter is to examine non-destructive testing methods that can be used in the field to evaluate the presence and effectiveness of silane sealers on the surface of concrete. These tests should be easy to use and give clear information about the silane at the concrete surface. Two different testing methods will be investigated. In Section 3.2 the Germann Water Permeability test was investigated and in Section 3.3 a surface resistivity test was used. For each of these tests their repeatability and reliability was investigated with concrete of different w/cm with and without silane.

3.2 Evaluation of GWT Unit

3.2.1 Overview

In this chapter the Germann water permeability unit (GWT) was investigated in hopes to develop a non-destructive methodology for ODOT to measure the efficiency of water proofing agents applied on concrete bridge decks. The instrument is developed by GERMANN INSTRUMENTS, INC for measuring water penetration in surface concrete and also for testing micro cracking of a concrete surface. In this study the apparatus is used to estimate the presence of water proofing solution by penetrating water through silane coated surface concrete under pressure. The penetration depth of pressurized water over time into saturated concrete can be estimated by Darcy's law (Jo-Hyeong Yoo, 2006).

A.I.Cark (1999) carried out an experimental study to determine the effect of silica fume and curing temperature on the permeability of concrete. In this study he used the GWT on the concrete cylinders to identify the permeability of concrete. However, his study did not investigate the consistency or variability of the measurements. In the current study water penetration was performed under a constant pressure with samples of different by taking water-cement ratio of the concrete as a variable. Based on the results obtained,

the reliability of the instrument is presented as well as a few modifications that may improve the method.

3.2.2 Experiment methods

3.2.2.1 Methodology

In the GWT, a sealed pressure chamber is attached to the concrete surface using anchors; the chamber is filled with water, and the required water pressure is applied to the surface. The amount of water penetrating the surface concrete is measured by keeping the pressure constant by using a micrometer gauge with an attached pin which substitutes the water leaving the chamber (Germann Instruments, 2010).

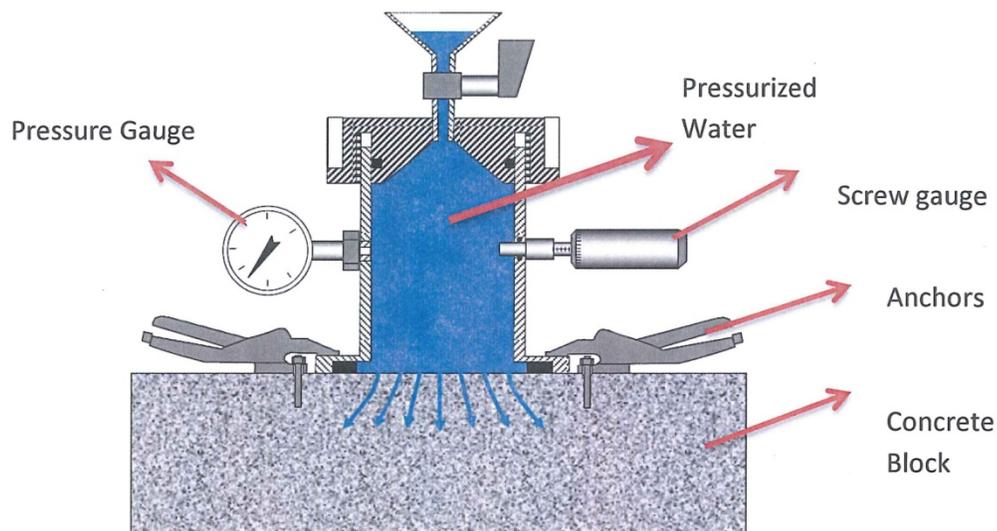


Figure 3.1: Cross-sectional view of GWT unit (image courtesy of Germann instruments)

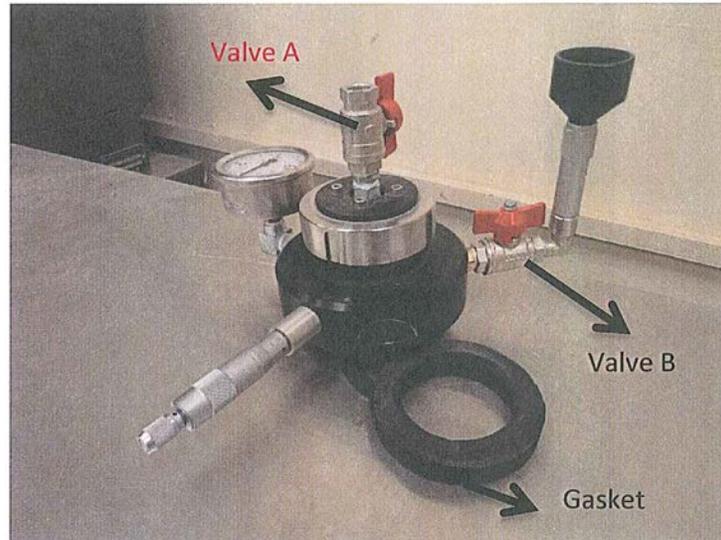


Figure 3.2: The GWT unit

For testing a horizontal surface, a water filling cup with an L-joint is attached to the valve B, as shown in Figure 3.2. The cup is turned so that it is pointing upwards and parallel to the other outlet valve of the pressure chamber (valve A). The lid is unthreaded so that 3-4 threads are visible and the micrometer gauge is set to an initial position. The gasket of 0.6" (15 mm) was used as an interface between the concrete surface and the apparatus. A wooden box with fixed anchors and a hole for the cylinder to sit in, as shown in the Figure 3.3, was built in the lab to conduct the experiments on the cylinders. Using the anchors, the housing is compressed fully against the water saturated concrete surface so that the gasket is invisible. The valves are closed and checked for any water leaks after filling them with boiled water. The lid is turned until the desired pressure is obtained. A pressure of 1 Bar was selected for all the results as recommended by Germann instruments. The selected pressure is maintained constant by turning the micrometer gauge clockwise, and gauge readings are noted every 10 minutes. Experiments were conducted for 15 minutes and 25 minutes but the change in flux was found to be similar. So, 10 different experiments were completed on each sample with water being forced into the concrete over a 10 minute period. The difference in the gauge reading is an index for the water penetration into the concrete. After testing if any water is visible on the surface under the compressed gasket this

means that water has escaped between the gasket and the concrete and the experiment must be repeated (Germann Instruments, 2010).



Figure 3.3: Wooden box with anchors fixed testing concrete cylinders.

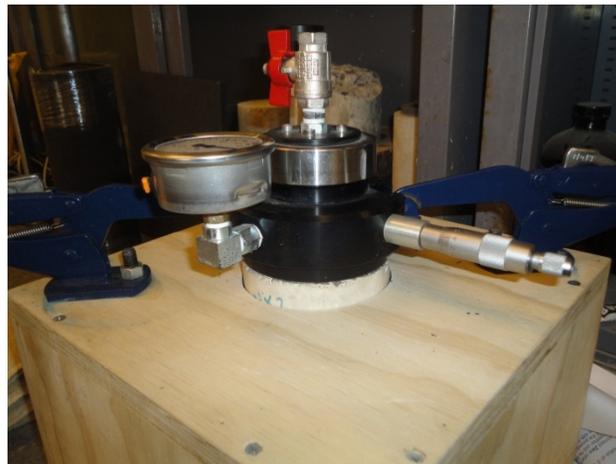


Figure 3.4: Conducting experiment on cylinder using GWT unit.

3.2.2.2 Material preparation

In this testing two different concrete mixtures prepared with water to cement ratios of 0.5 and 0.7 were prepared. These ratios resulted in two different sets of samples with an ample difference in their permeability. The cement used for these mixtures is an ASTM C 150 type I/II cement. A summary of these mixtures is given in Table 3.1. For every batch of concrete, 20 cylinders were prepared. All the cylinders were cured in a fog room for 7 days and later dried in a chamber room with a temperature of 73°F and

40% relative humidity for 20 days. After 27 days of curing. The flat surfaces of the cylinders were lapped with 80 grit pads to remove any residue and to make sure that the surface is level with no cracks. Later, the cylinders are submerged in water until a steady weight is obtained and then they are tested with the GWT unit.

Table 3.1: Concrete mixture proportions

Cement (lbs/yd ³)	CA (lbs/ yd ³)	FA (lbs/ yd ³)	Water (lbs/ yd ³)	w/cm
611	1850	1290	306	0.5
564	1755	1063.7	395	0.7

3.2.2.3 Application of Silane and Depth of Penetration

The silane used in this experiment is SIL-ACT ATS-42 from Advanced Chemical Technologies of Oklahoma City. Cylinders were submerged in silane for 20 minutes and allowed to dry for 24 hours before testing. By trial and error method it was found that after 20 minutes of submerging the 0.5 w/c concrete had a depth of silane penetration of 1/8". To simplify the tests the same time of ponding was used for the 0.7 w/c concrete.

After measuring the flux of the surface concrete coated with silane, the cylinders are split and are dipped into colored dye to measure the average depth of penetration. The concrete dipped in dye is shown in the Figure 3.5.

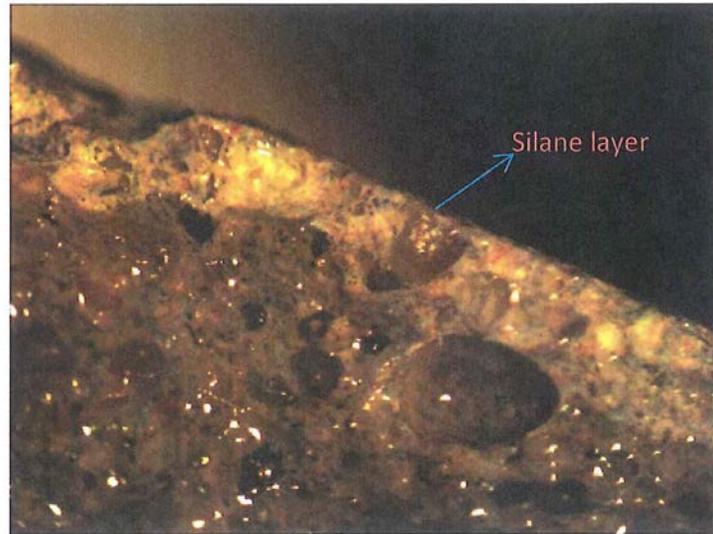


Figure 3.5: Light microscope image of concrete that has been placed in dye to show the layer of silane on the surface of the cylinder

3.2.2.4 Evaluating the Test Results

The initial and final readings of the micrometer gauge are noted over a period of time, and the flux Q is calculated for a given water pressure as

$$Q = B \cdot (g_1 - g_2) / (A \cdot t)$$

Where g_1 and g_2 are final and initial reading measured on the micrometer gauge in inches and t is the time of the test performed in seconds. B is the area of the micrometer pin that substitutes water leaving the chamber. The diameter of the micrometer pin used in the GWT unit is 0.394" (10 mm). Therefore area " B " is 0.122 in² (78.6 mm²). A is the area of the concrete pressurized which is 4.678 in² (3018 mm²) (Germann Instruments, 2010). Therefore the flux q is $Q = 0.026 \cdot (g_1 - g_2) / t$ inches per second.

3.2.3 Results

Tests are conducted on both 0.5 and 0.7 water-cement ratio concrete with and without silane applied using a GWT unit. The test results are compared to determine the accuracy and repeatability of this technique.

The water flux for 0.5 and 0.7 concrete before and after application of silane are calculated and shown in Figure 3.6. The flux for individual specimen is the average of 10 measurements and the average flux is the average of all the three respective cylinders.

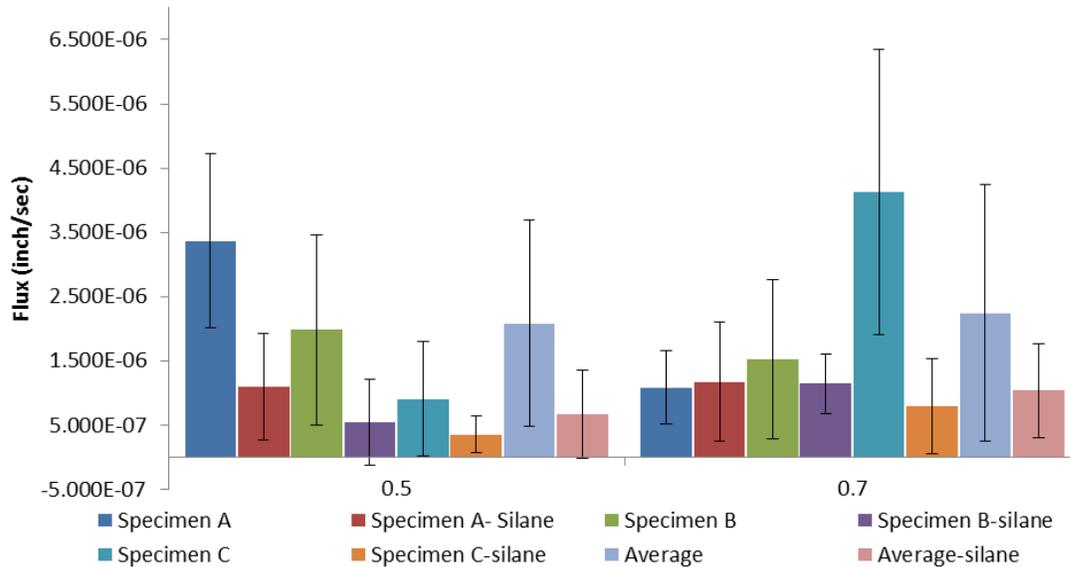


Figure 3.6: Flux results on 0.5 and 0.7 concrete with their averages

3.2.4 Discussion

3.2.4.1 Uncoated Concrete Cylinders

From the results obtained in Figure 3.6, it can be seen that the standard deviation of the measurements is very high for every cylinder. The high standard deviation means that the results are inconsistent. The surface water absorption for both 0.5 and 0.7 w/cm concrete has nearly identical values, and a huge overlap of the range of flux is observed. However, it would be expected that the 0.7 w/cm would have an exponentially higher permeability than 0.5 w/c concrete as shown in the Table 3.2 (Kosmatka, 2002). This data implies that this testing device has too much variability to accurately determine the difference in permeability between concrete with 0.5 and 0.7 w/cm.

Table 3.2: Permeability of concretes moist cured 7 days and tested after 90 days (Kosmatka, 2002)

<i>Water-cement Ratio</i>	<i>Permeability</i>	
	<i>ASTM C1202 (RCPT, Coulombs)</i>	<i>API RP 27 (Water, in/s)</i>
0.50	4315	7.64×10^{-8}
0.60	4526	8.78×10^{-8}
0.75	5915	32.76×10^{-8}

3.2.4.2 Silane Coated Cylinders

Measurements are taken on silane coated cylinders to observe if the instrument can differentiate the surface water penetration for the cylinders with and without application of silane. In Figure 3.6 again it can be seen that the standard deviation of the measurements were very high. However in all cases it appears that the silane treatment did reduce the average measured permeability. Unfortunately, since the standard deviations are so high, it would take a large number of measurements to determine this information. For concrete with 0.5 w/cm ratio, the application of silane reduced the surface penetration by 60 to 70% and for concrete with 0.7 w/c showed either no change or a decrease. It does appear that the GWT is capable of determining the difference in the water penetration between normal concrete and silane coated concrete, but the measurements are very inconsistent. While it may be possible to measure concrete before and after it has been treated with silane and determine the presence and effectiveness of the silane, this does not seem convenient to evaluate silane coatings for field concrete. Also, because of the significant inconsistencies in the measurements with the devices, it was decided that the GWT is not recommended to evaluate the performance of silane coatings on field concrete.

3.2.4.3 Possible Reasons for the Inconsistency in the Data

Water was found on the edges of the gasket if the experiment is left under pressure for 30 minutes or sometimes more. Therefore the probable reason for the observed

inconsistency might be the improper interface between the gasket and concrete allows water to escape between the interface of the gasket and the concrete.

Some possible modifications to the apparatus include gluing a plastic O-ring with an inner and outer diameter the same as that of the gasket to the surface of the concrete. The apparatus should be placed on the plastic O-ring to conduct the experiment. This would prevent water from escaping from the interface between the concrete and the gasket. The gasket could also be replaced with soft neoprene or rubber which can be better compressed to the surface of the concrete. Neither of these techniques were tried in this work but might make the device useful for future applications.

3.2.5 Conclusion

The objective of this work is to develop a non-destructive approach for finding the presence of silane using the GWT apparatus. The experimental results in this study show that this technique has proven to have a high variability in its measurements in laboratory testing where a special frame was used to consistently connect the apparatus to the surface of concrete. The apparatus was not able to determine the difference between concrete without silane that had significantly different w/cm (0.5 and 0.7) and therefore different permeability. The system was able to measure the reduction in permeability from the application of a silane sealer if a measurement could be taken before and after the silane application. The method was not recommended for field use because of its high variability and the inconvenience of having to measure the concrete prior to the application of the silane.

3.3 Identification of Silane on Concrete Using the Four-Point Wenner Probe Method

3.3.1 Overview

The focus of this research is to develop a methodology to identify the presence of silane on concrete using the four-point Wenner Probe Method. Concrete resistivity is affected by water-cement ratio, moisture content (degree of saturation) and degree of hydration. It varies over a wide range from 1 to 104 k Ω .cm (Polder, 2001). In past, researchers

were successful in proving that the concrete resistivity measurements of a saturated concrete is an indicator of permeability (Kessler, 2005). N.S. Rengaswamy et al. (1986) in his research states that four point resistivity meter is a useful nondestructive technique to assess the quality of concrete and also explains that the porosity of the dry and wet concrete can be assessed by measuring the resistivity of concrete. In dry concrete, the voids are filled with air and so it is more difficult for current to pass through the concrete. This makes the resistivity of dry concrete high. For wet concrete, the pores are filled with water and this establishes electrical connectivity for the current to pass. So, the resistivity of wet concrete is lower compared to that of dried concrete. In this paper, a study is conducted to understand the change of concrete resistivity for different w/c ratios with and without silane and with changes in moisture content. Correlating these results a method for identifying the presence of silane is proposed.

3.3.2 Methodology

3.3.2.1 Material Preparation

For this testing four different concrete mixtures were created with water-cement ratios of 0.35, 0.4, 0.5 and 0.7 producing samples with significant differences in their permeability. The cement used for these mixtures meets ASTM C 150 type I/II cement and the rock and sand are commonly used in transportation construction in Oklahoma. A summary of these mixtures are given in Table 3.3. For every batch of concrete 20 cylinders were cast and cured in the fog room for 7 days and later dried in a chamber room with temperature 73⁰ F and 40% relative humidity for 20 days. After 27 days of curing. The surface of cylinders were ground with 60 grit sand paper (as shown in the Figure 3.7) to remove any residue and dirt before testing the resistivity.



Figure 3.7: Sand grinding the surface of the concrete cylinder

Table 3.3: Mixture proportions

<i>Cement</i> <i>(lbs/yd³)</i>	<i>CA</i> <i>(lbs/ yd³)</i>	<i>FA</i> <i>(lbs/ yd³)</i>	<i>Water</i> <i>(lbs/ yd³)</i>	<i>w/cm</i>
611	1875	1375	214	0.35
611	1755	1325	245	0.40
611	1850	1290	306	0.50
564	1755	1063.7	395	0.70

3.3.2.2 Test Methods and analysis of test results

In this paper, the resistivity of the concrete is measured using two methods Two Plate Resistivity Method and four-point Wenner probe method.

3.3.2.2.1 Two Plate Resistivity Method

In this method, the cylindrical concrete specimen is placed in between two metal plates via wet sponge as an interface between the flat concrete surface and the metal plates as shown in the Figure 3.8. The resistance between the two plates is measured and the resistivity is calculated by

$$P_{\text{concrete}} = R_{\text{Measured}} * A/L$$

Where:

P_{concrete} = Resistivity (kohm-cm)

R_{Measured} = Resistance Measure (kohm)

A = Area of the circular face (cm²)

L = Length of the cylinder (cm)

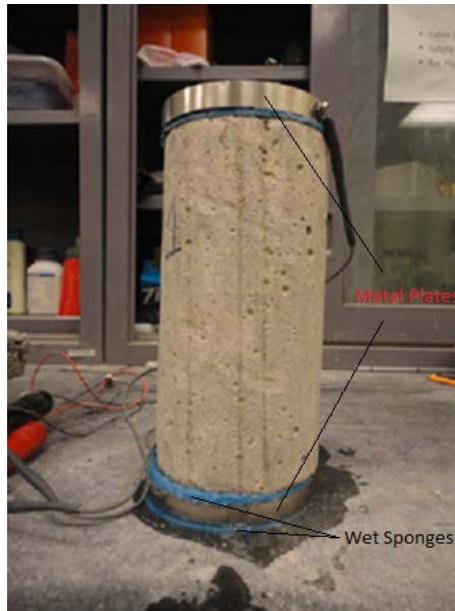


Figure 3.8: Measuring the resistivity of concrete by two-plate resistivity method.

3.3.2.2.2 Four-point Wenner probe method

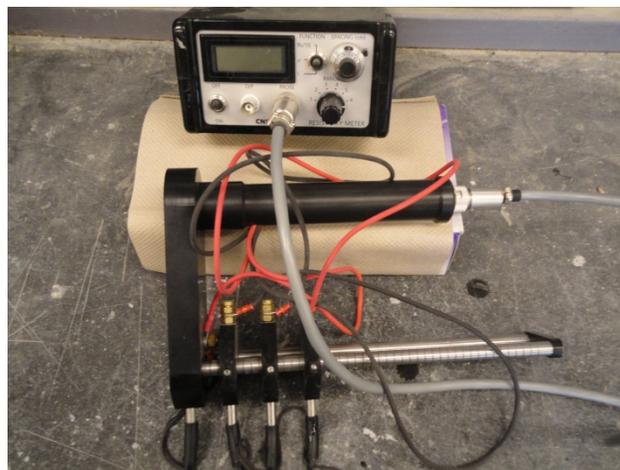


Figure 3.9: The four-point Wenner resistivity meter.

In this method, four equally placed point electrodes with water saturated wooden tips are pressed on to the concrete face longitudinally (as shown in the Figure 3.11) and a

small ac current(I) is passed through outer contacts and the resultant potential difference (v) between the inner contacts is measured. The apparent resistivity is measured from the resistivity meter using the equation $\rho_{app} = 2\pi a \frac{v}{I}$, where “a” is the probe spacing.

A total of eight reading are taken at different spots for each cylinder and the spots are marked as shown in the Figure 3.10a&b.



Figure 3.10a&b: Cylinder with spots marked at the places where resistivity is measured.

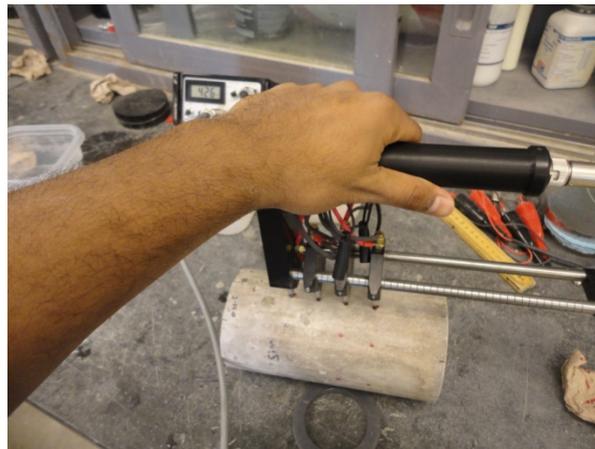


Figure 3.11: Resistivity measured using the Wenner four-point probe method.

Calculation of exact resistivity

If the probe is applied to a wide concrete slab with thickness much larger than the probe spacing and there is no interference from the reinforcing steel, then $\rho_{app} = \rho$. For smaller

bodies such as the concrete cylinders, a cell constant correction K can be defined such that (Morris et al., 1996)

$$\rho = \rho_{app} / K$$

Where:

ρ = exact resistivity

ρ_{app} = apparent resistivity measured by four-point probe

K = cell constant, function of probe spacing "a" and geometry of the specimen

Calculation of Cell Constant (K)

The cell constant correction is determined from the graph below suggested by Morris (1996). These values were determined through a combination of experiments and finite element analysis.

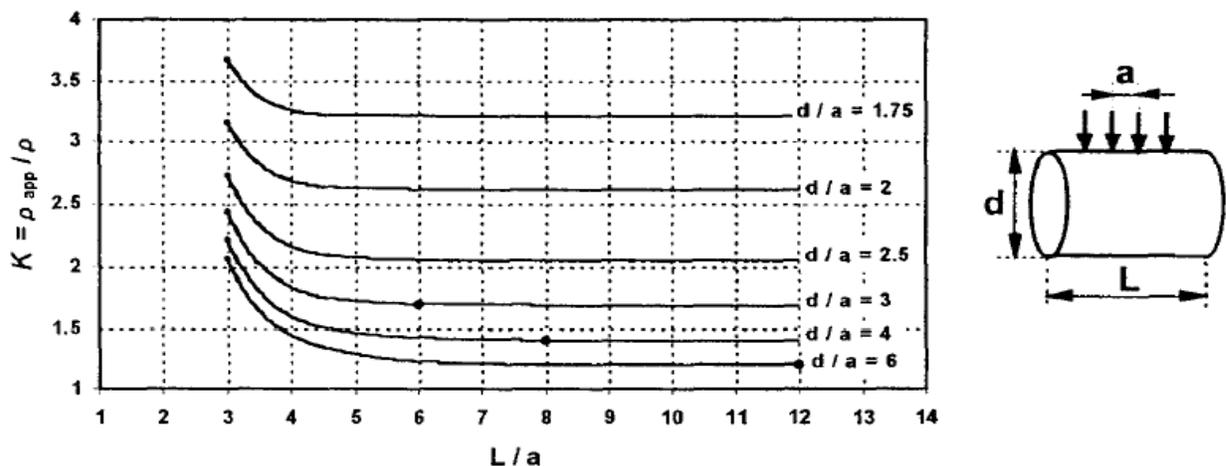


Figure 3.12: Cell constants versus L/a (Morris, 1996)

For cylinders of size 4"x8" and probe spacing of 1", the value of cell constant correction (K) is determined to be 1.41.

Experimental Method

Three concrete cylinder samples from each concrete mixtures of different w/cm of 0.35, 0.4, 0.5 and 0.7 are taken and submerged in water until the weight remains constant. Concrete resistivity of the cylinders is measured using both the two plate method and the four-point Wenner probe method.

Also, six cylinder samples from each mixture (with w/c ratio 0.35, 0.4 and 0.5) are taken and oven dried at 110⁰C until there is no change in weight of the cylinders and the cylinders are left to cool down under room temperature. Of these six cylinders, three were silane coated and three were left uncoated from each mixture. The weight and resistivity of the cylinders are measured over time by submerging them in water until the measurements were constant. Total of eight resistivity measurements are taken for each cylinder as shown in Figure 3.10. It is also observed that the measurements taken on dry concrete are highly unstable and takes 4-5 minutes to stabilize.

3.3.2.3 Application of Silane and Depth of Penetration

The water proofing solution, silane used in this experiment is SIL-ACT ATS-42 from Advanced Chemical Technologies, Oklahoma City. All cylinders were submerged in silane for 20 minutes and allowed to dry for 24 hours before testing. To simplify the testing a constant amount of ponding time was used for all of the tests. The difference in w/cm for the concrete would be expected to cause different depth of penetrations with less depth of penetration for lower w/c concrete. This helps to determine the effect of depth of penetration of silane on the concrete resistivity.

After measuring the resistivity of the concrete coated with silane, the cylinders were broken in half and stained with colored dye to differentiate silane coated concrete from normal concrete. The depth of silane penetration is measured using calipers.

3.3.3 Results

The resistivity measured by two-plate resistivity method and Wenner probe method for saturated concrete with different water –cement ratios are compared and are presented in Figure 3.13.

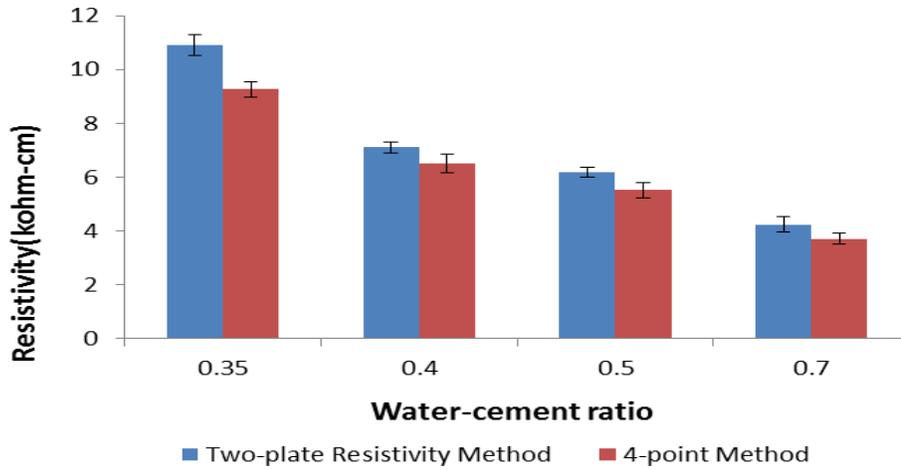


Figure 3.13: Comparison between resistivity method and Wenner probe method

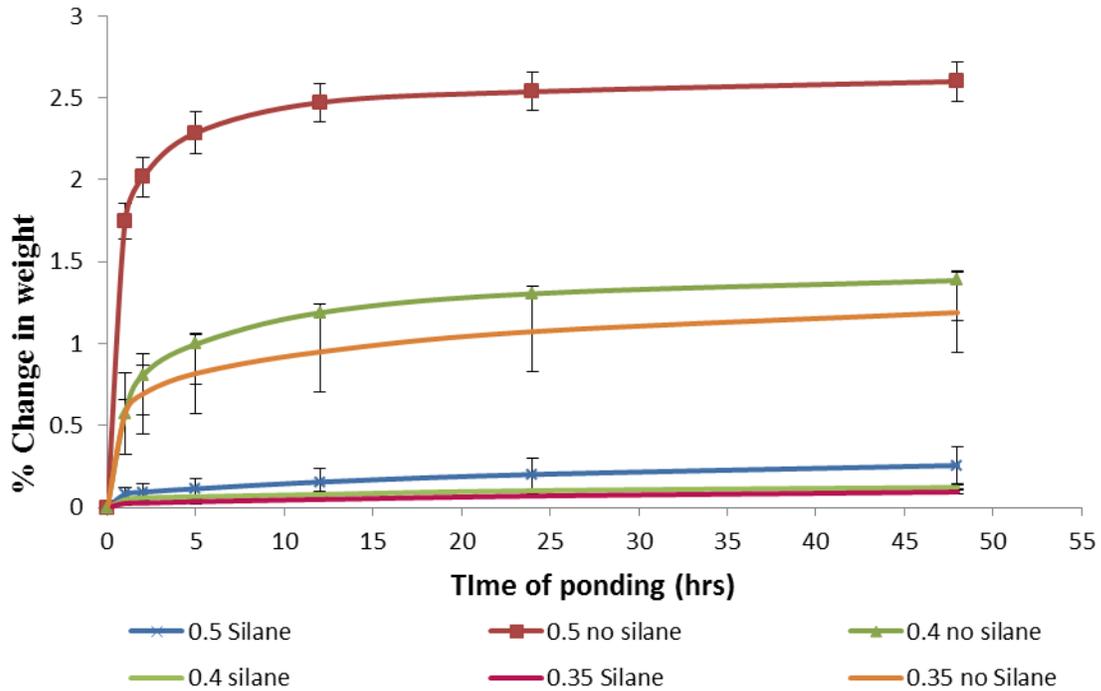


Figure 3.14: Time of ponding vs. Change of weights

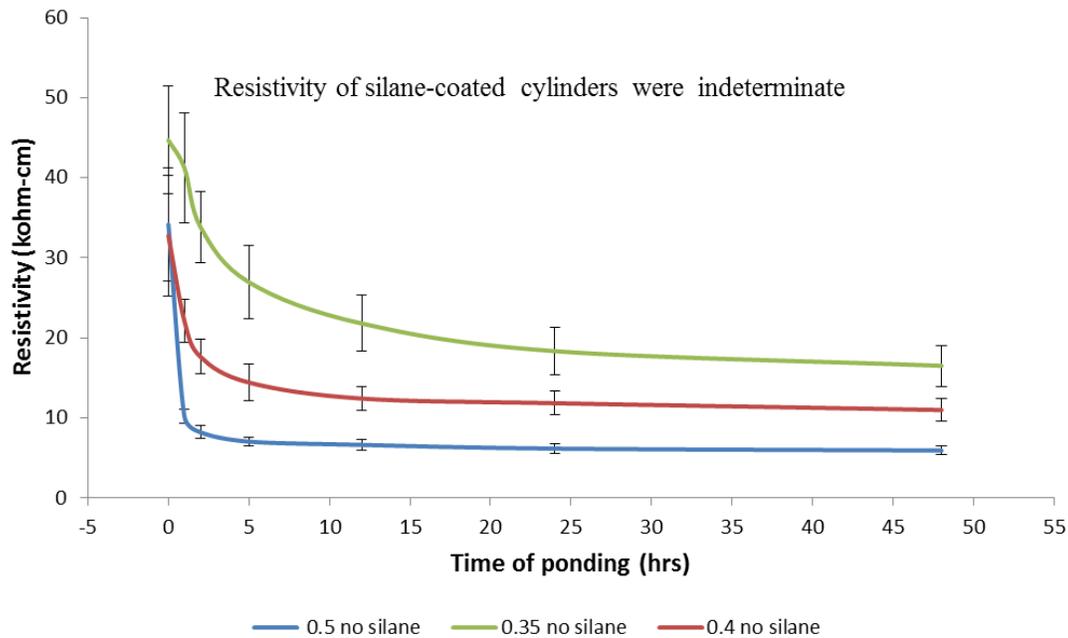


Figure 3.15: The measured resistivity is shown versus the time of ponding.

The measured average depth of penetration of silane in concrete with different w/c ratio is presented in Table 3.4. Each measurement is the average of 45 readings with 15 measurements from each cylinder.

Table 3.4: The depth of silane penetration in concrete of different w/cm.

<i>w/c ratio</i>	<i>Depth of Penetration (inches)</i>		
	<i>Average</i>	<i>Standard Deviation</i>	<i>Coefficient of Variance</i>
0.70	0.18	0.11	0.58
0.50	0.09	0.06	0.59
0.40	0.08	0.04	0.51
0.35	0.06	0.04	0.58

3.3.4 Discussion

In Figure 3.13, it is shown that the resistivity of the concrete measured by the Wenner probe method is similar to the resistivity measured by the two plate method. The low standard deviation of the measurements shows the high precision of the tests on

saturated concrete. The classification of 28 day resistivity of saturated concrete for different w/c for the four-point Wenner probe is as follows for the limited specimens investigated:

Table 3.5: Classification of resistivity for variable w/c ratio concrete

w/c ratio	Resistivity (kΩ-cm) for a=1 inch
0.35	8-10
0.40	6-8
0.50	5-6
0.70	3-4

These results show that both the Wenner probe method and the two plate resistivity method could be used to find the resistivity that should give an indication of the permeability of saturated concrete.

In Figure 3.14, it is observed that the change in weight increase of concrete was significantly reduced after the application of silane. Also, it is observed that for normal concrete, the maximum change in weight was in the first hour and becomes constant over time.

In Figure 3.15, the results show that the resistivity is high and more variable for dry concrete and decreases with the increase in moisture content. Since the pores in wet concrete are close to saturation the resistivity of wet concrete is lower compared to that of dry concrete. It should also be noted that it was not possible to obtain a reading for the cylinders that had been coated with silane due to high contact resistance between the surface layer and the probes. The resistivity of the concrete coated with silane, regardless of the w/cm, was shown to be out of range or with high instability. In Figure 3.15, it can be seen that the standard deviation of the measurement decreased as the increase in moisture content. “If the concrete has recently been wetted or is drying out

after a period of saturation, then there will be effectively layers of concrete with different resistivity values” (Concrete Resistivity Manual, 2008). This could be an explanation for the reason the variability in measurements for moist concrete compared to saturated concrete.

In Figure 3.15, it is also observed that regardless of the w/cm, the resistivity of concrete significantly dropped in the first two hours and then slowly decreases over time. This is because the rate of absorption of water by concrete is high initially (from Figure 3.14). From the data it can be seen that when the concrete is dry the resistivity measurement with the Wenner probe will be high with or without silane. If the concrete surface absorbs water then the resistivity measured by the Wenner probe will also decrease. However, only concrete that does not have an effective layer of silane on the surface would be expected to allow water to absorb over time. Since this absorption can happen in a very short period of time the Wenner probe could be used on a bridge deck before and after a short ponding period. If the resistivity changes over this period then it must be due to water penetration into concrete with an ineffective silane layer.

3.3.5 Proposed Method

By correlating the results in Figure 3.14 and 3.15, a non-destructive field method is proposed for finding the presence of silane in concrete.

An area to be tested is selected on the bridge deck which was not affected by any moisture for past 7 days to make sure it is dry and scrubbed without using water to remove any oil or dust present on it. A square grid of 4”x 4” is marked with sixteen nodes placed equally spaced one inch apart making a total of eight readings with four in horizontal direction and four in vertical direction as shown in figure below.

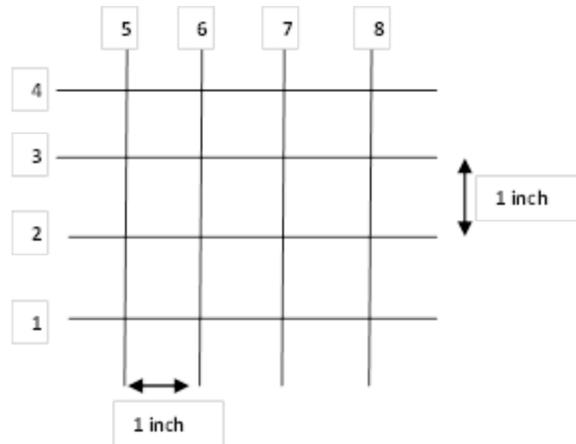


Figure 3.16: Sample proposed grid for measurements

The resistivity is measured with the Wenner four-point probe on each line with the probes at each node. Next a cylindrical frame with open end on both sides is placed on the grid such that whole grid is covered as shown in Figure 3.17. The frame is filled with water and left undisturbed for 45-60 minutes. The frame is removed and the surface is wiped with a towel to remove any water on the surface. The resistivity is measured at the same spots with Wenner probe and compared with the previously measured results (as shown in Figure 3.18). If there is silane present on the surface of the concrete then resistivity of the first reading should be high and remain high after the water is ponded on the surface. If silane is not present then the resistivity should decrease in the concrete between the initial measurement and after it was ponded. The concrete investigated in this test should not be exposed to water or a rainfall for at least the previous 24 hours.

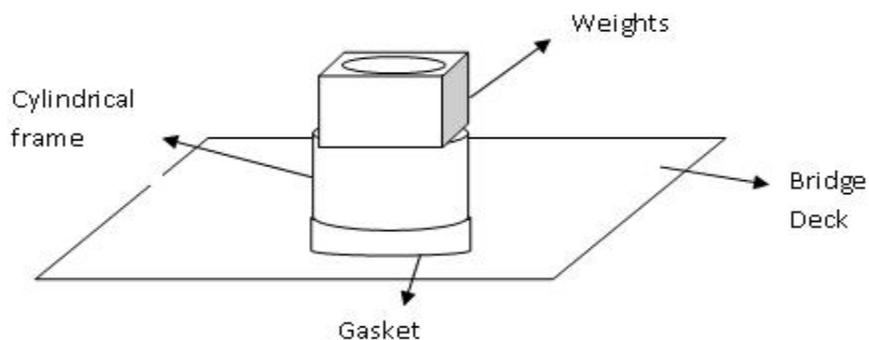


Figure 3.17: Schematic representing on site arrangement

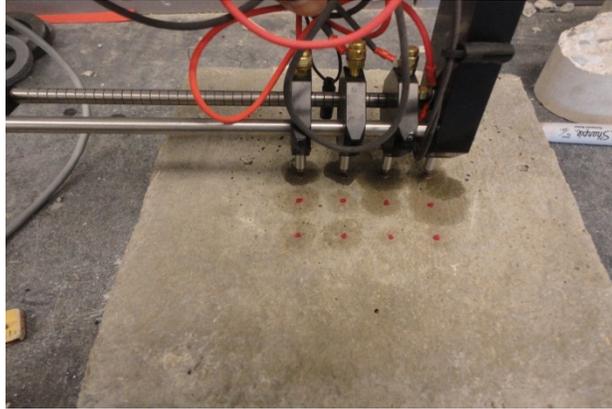


Figure 3.18: Measuring resistivity of flat surface concrete

3.3.6 Conclusion

Concrete resistivity was measured using the two plate resistivity and the Wenner probe method for w/cm of 0.35, 0.4 and 0.5 concrete and the results were compared. These results concluded that both methods are reliable and provide close results that give a relative indication of the permeability of concrete. Because of this the Wenner probe appears to be a promising tool to investigate field concrete.

The resistivity of concrete that was dry or contained a silane coating was found to be difficult to measure due to high contact resistance between the concrete surface and tips of the probe. Furthermore, it was shown that the resistivity of the dry concrete decreased as water was absorbed. Using this information, a field test method was proposed that uses a resistivity measurement before and after a wetting period for concrete to determine if an effective silane coating is on the surface.

3.4 Conclusions

The goal of this work is to find a non-destructive technique to identify the presence of silane on the surface of concrete bridge decks. Two different techniques used to finding the permeability of concrete that are currently commercially available are reviewed and tested to understand the repeatability and relative accurately with concretes of different w/cm and with and without silane. The finding and recommendations are as follows:

3.4.1 Germann Water Permeability Test

The experimental study of this apparatus shows that this test is highly variable. The large variance in the measurements makes it complicated to understand the results of

the test. The results could also be widely affected by various parameters such as the anchor force, gasket type and surface of the concrete tested. Though, the apparatus was successful in showing the difference in the water absorption of surface concrete with and without silane, the reliability is too low due to the high standard deviations. Also one would have to have original measurements of water permeability of the concrete before the silane is applied to determine the difference which may not be practically possible.

3.4.2 Four-Point Wenner Probe Resistivity Method

The laboratory phase of this study showed that this technique is quick, reliable and accessible. Tests are conducted with four-point Wenner probe resistivity meter on concrete cylinders with different water-cement ratios and are compared with two-plate resistivity method. Both results were found to be comparable and to have a low variance.

The change in resistivity for normal concrete with change in degree of saturations was also observed. The high surface resistance of the concrete with silane makes the resistivity of the silane applied concrete immeasurable. A simple field method is proposed to find the presence of silane sealer on a bridge deck based on the measurement of the change in resistivity of the concrete before and after being ponded with water.

3.5 Using Micro X-ray Fluorescence (μ -XRF) to Investigate Silane in Concrete

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

3.5.1 Micro X-ray Fluorescence (μ -XRF)

Micro X-ray Fluorescence (μ -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 3.19.

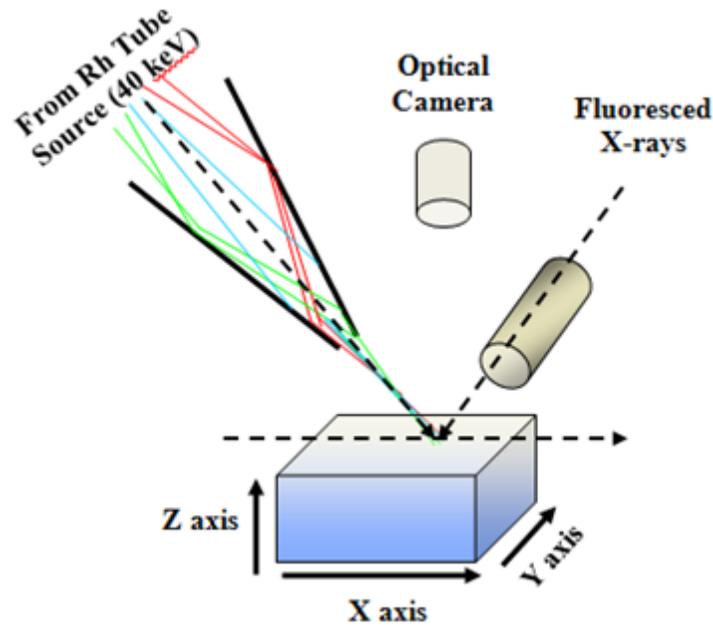


Figure 3.19: A diagram of a typical μ -XRF.

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 μ -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, μ -XRF uses an x-ray optic to focus x-rays down to a spot size of 50 μm . 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, μ -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 3.20. The concrete sample shown in Figure 3.20, demonstrates the μ -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.

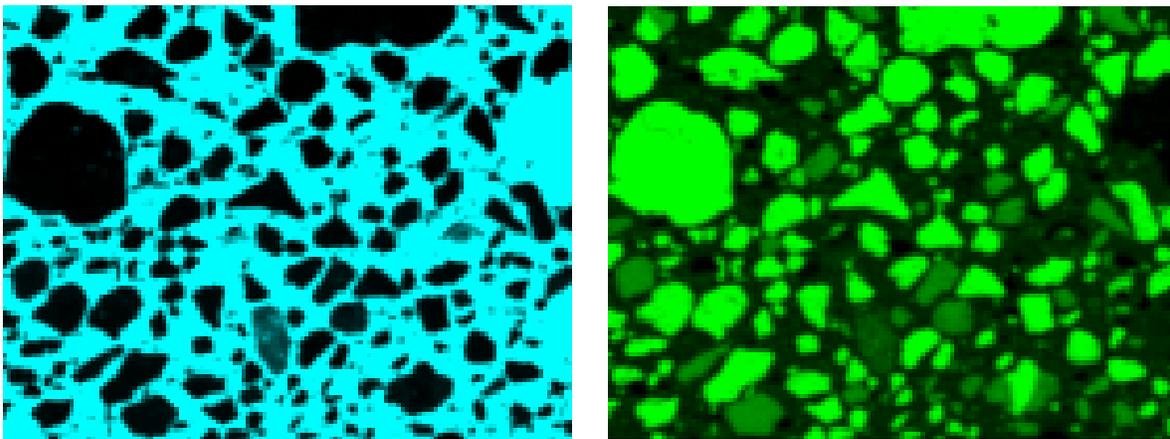


Figure 3.20: (left) elemental calcium image and (right) elemental silicon image

3.5.2 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 3.21.

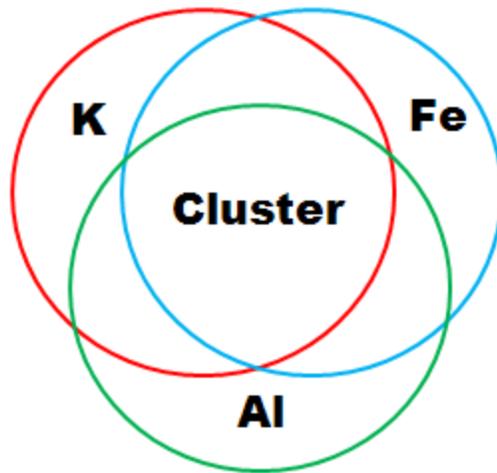


Figure 3.21: A cluster defined by aluminum, iron, and potassium

This process is repeated until the entire surface has been defined (i.e. multiple clusters). Then a cluster map, like that shown in Figure 3.22, 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 3.22 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.

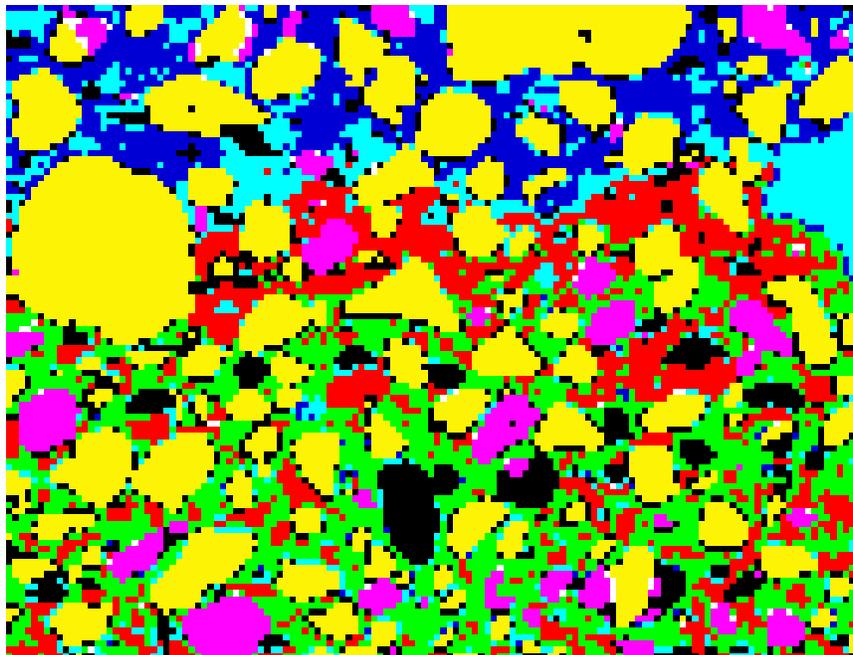


Figure 3.22: An example of a cluster map.

3.5.3 Using μ -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 μ -XRF displays a few chemical clues that could help to identify the presence of silane. One of these clues, as shown in Figure 3.23, was a noticeable high band of sulfur (i.e. bright blue pixels) which was found just below the silane boundary.

Figure 3.23: 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 3.24. The silane boundary has been highlighted with a yellow line.

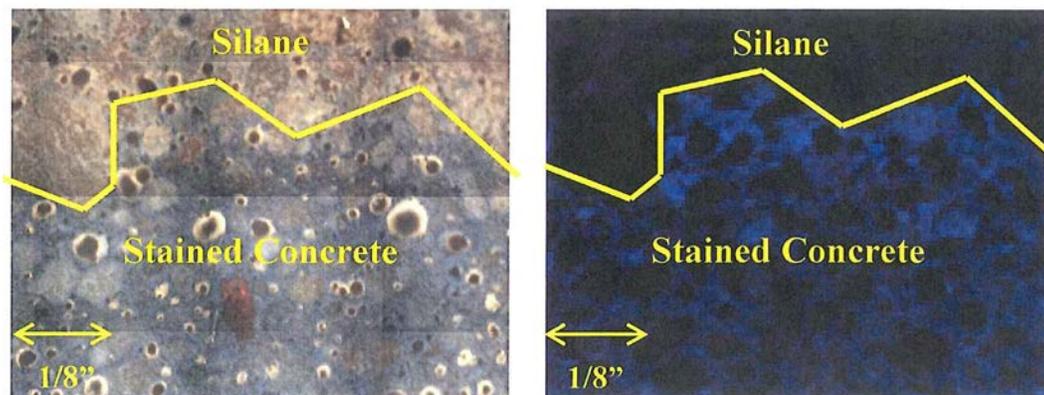


Figure 3.24: (left) optical image with colored dye and (right) elemental sulfur image from the mXRF.

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 3.25.

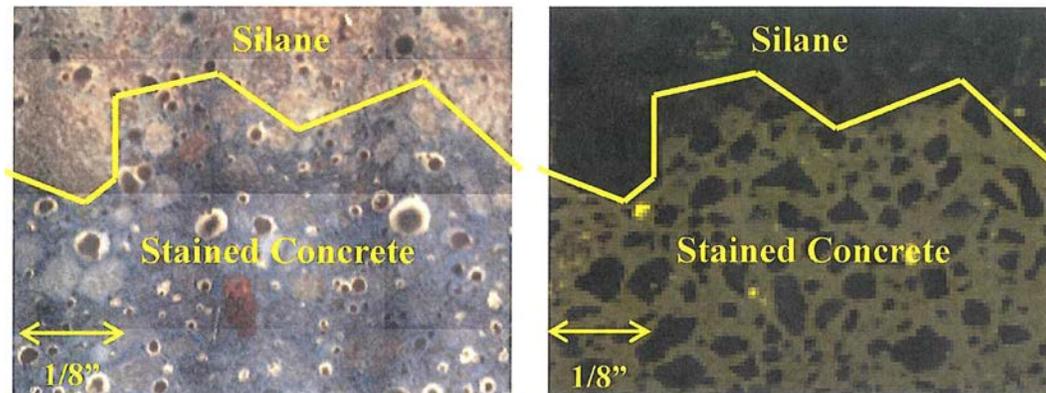


Figure 3.25: (left) optical image with colored dye and (right) elemental chlorine image from the mXRF.

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 3.26. The high sulfur concentration band that was found just under the silane boundary in Figure 3.23 is represented by an area of dark blue in Figure 3.26. 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 3.23 and 3.24 has been highlighted by a red line in Figure 3.26.

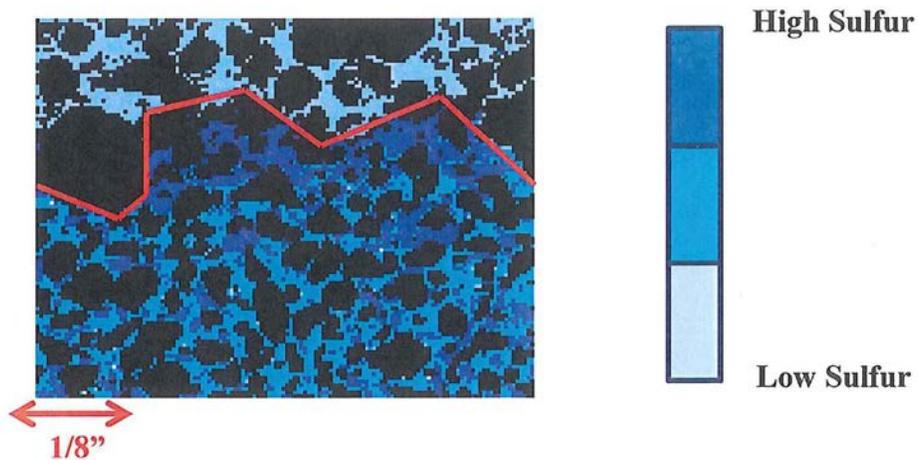


Figure 3.26: The segmented cement paste cluster map based on varying sulfur concentrations.

These observations demonstrate the μ -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.

3.5.4 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 μ -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 3.27, and then scanned using μ -XRF.

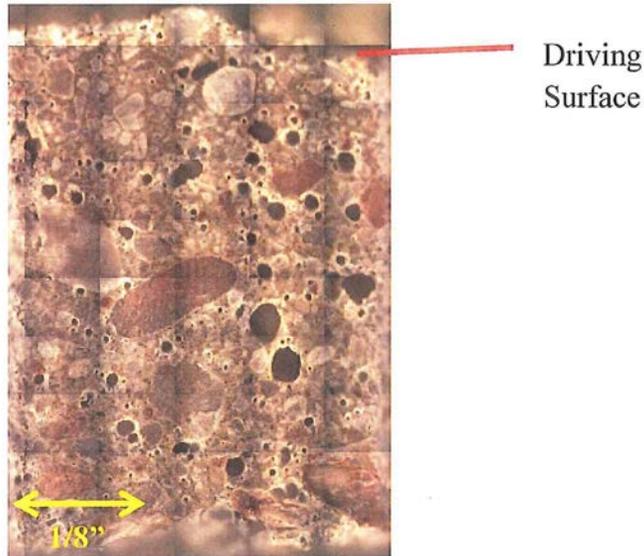


Figure 3.27: An example of a core sample that has been polished through the depth.

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 3.28, 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 3.28.

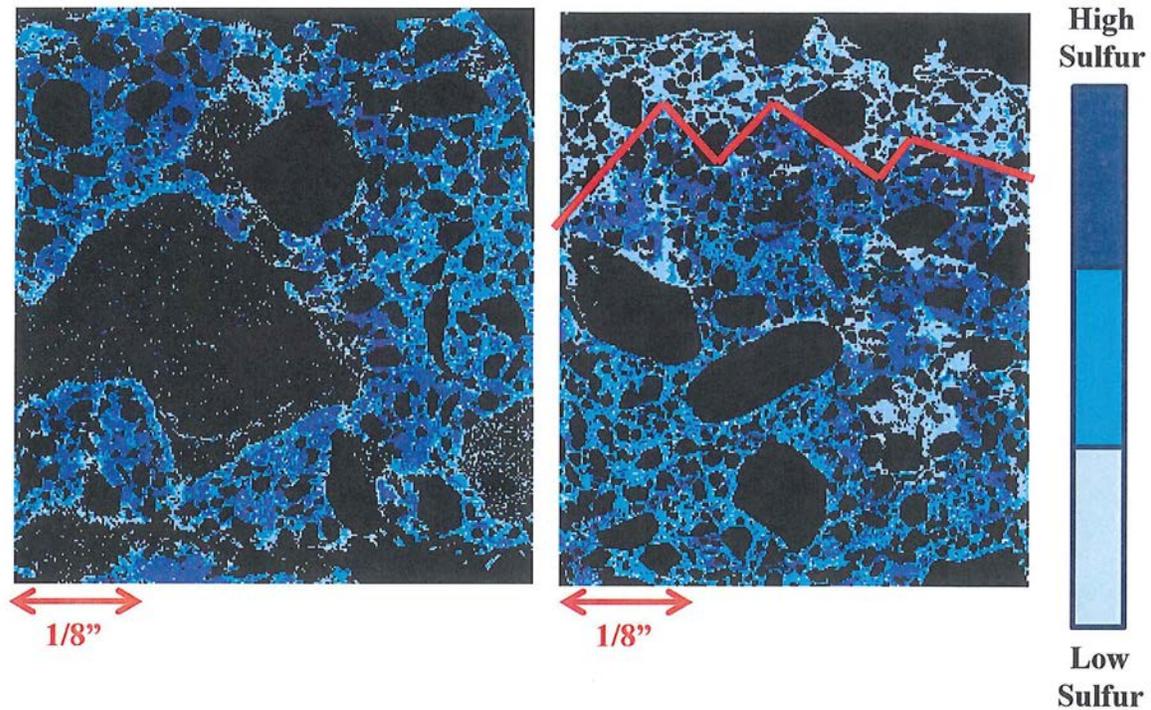


Figure 3.28: (left) cement paste cluster map with no band of sulfur (right) cement paste cluster map with a band of sulfur. The sulfur band has been shown to correspond to the presence of silane.

3.5.5 Chlorine Based Dyed

In addition to μ -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 μ -XRF. Again, 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 3.29.

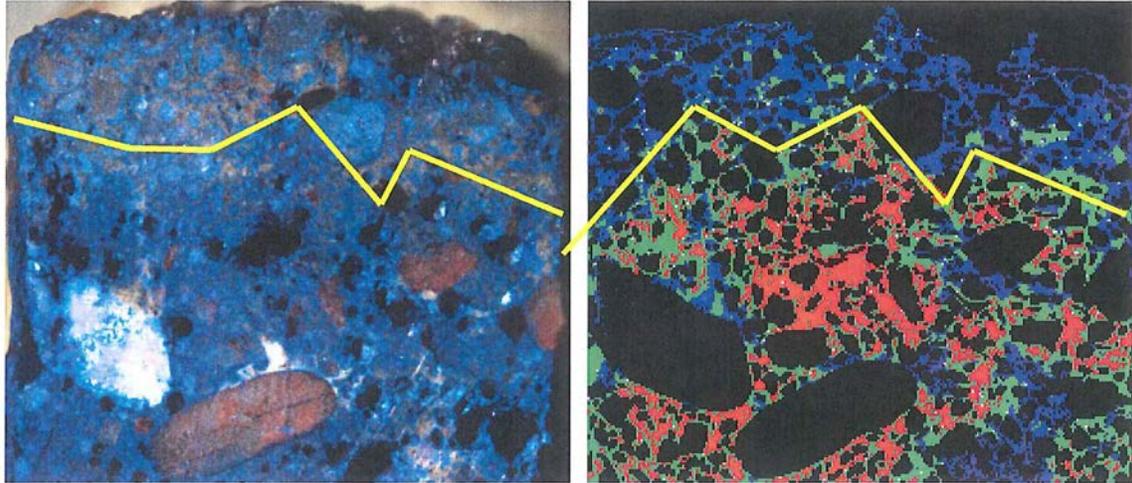


Figure 3.29: (left) optical image of core after ponding in chlorine based dye (right) chlorine based cement paste cluster map

3.5.6 Results

The chemical clues provided by μ -XRF as well as the chlorine based colored dye were used to determine the presence of silane in all field core samples. Table 3.6 is a summary of the results of each technique used on each sample to determine the presence of silane.

Table 3.6: 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 μ -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 μ -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.

3.5.7 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 3.30 and 3.31, respectively, where the suggested silane boundary in the chlorine image is highlighted by a red line.

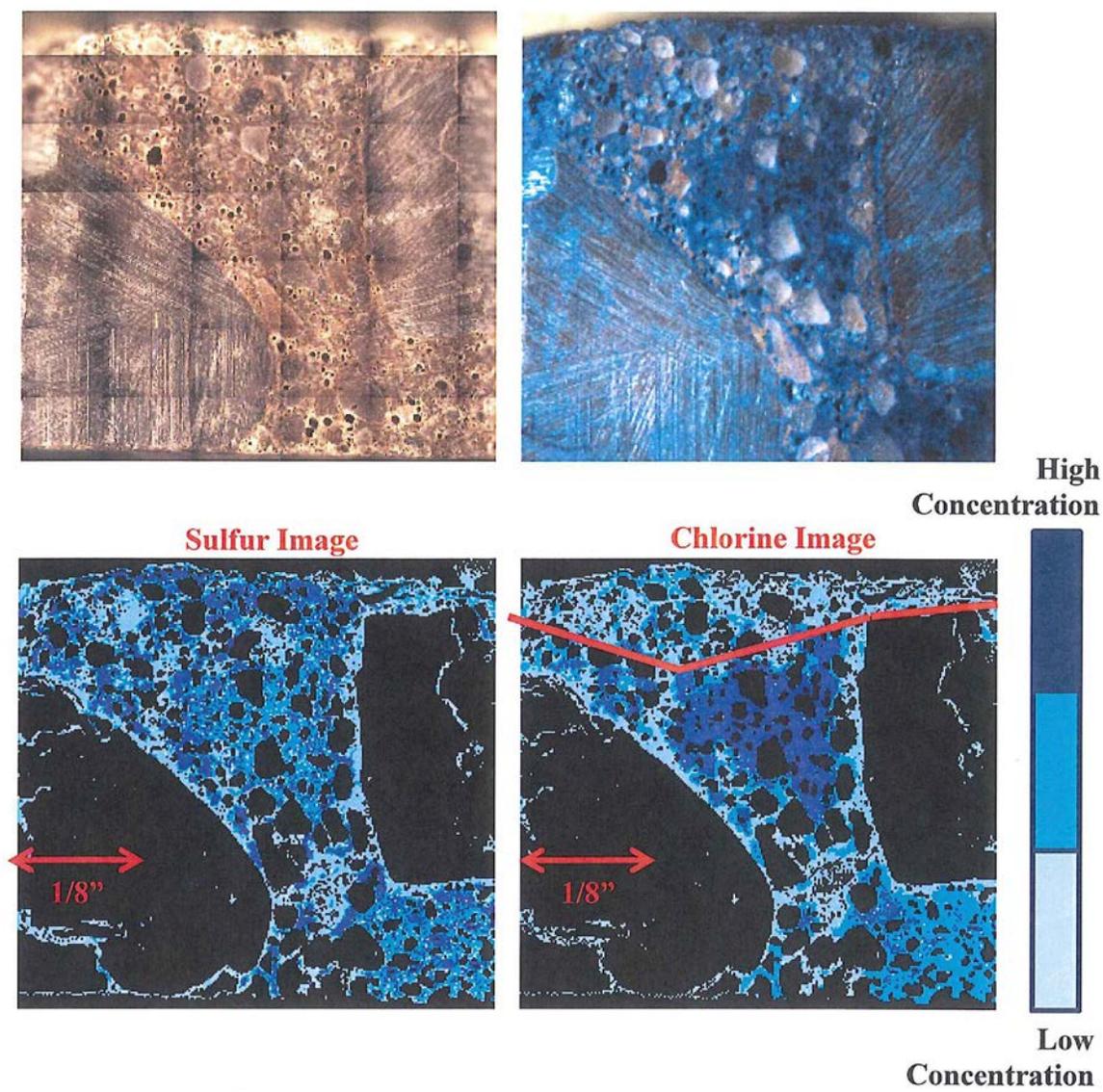


Figure 3.30: SH3 #2 sample (top left) non-dyed optical image (top right) optical image of dyed sample (bottom left) segmented sulfur image (bottom right) segmented chlorine image

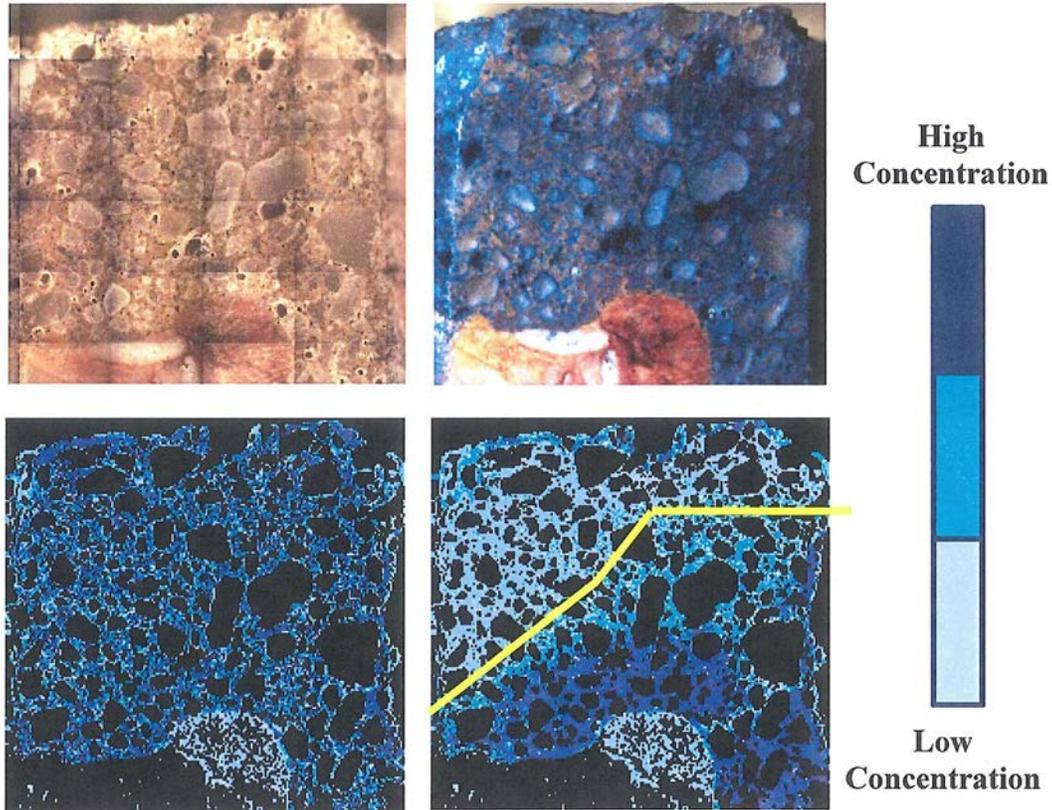


Figure 3.31: US62 #2 sample (top left) non-dyed optical image (top right) optical image of dyed sample (bottom left) segmented sulfur image (bottom right) segmented chlorine image

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 Figures 3.33, a crack provides a direct pathway for chlorides to diffuse deeper into the concrete.

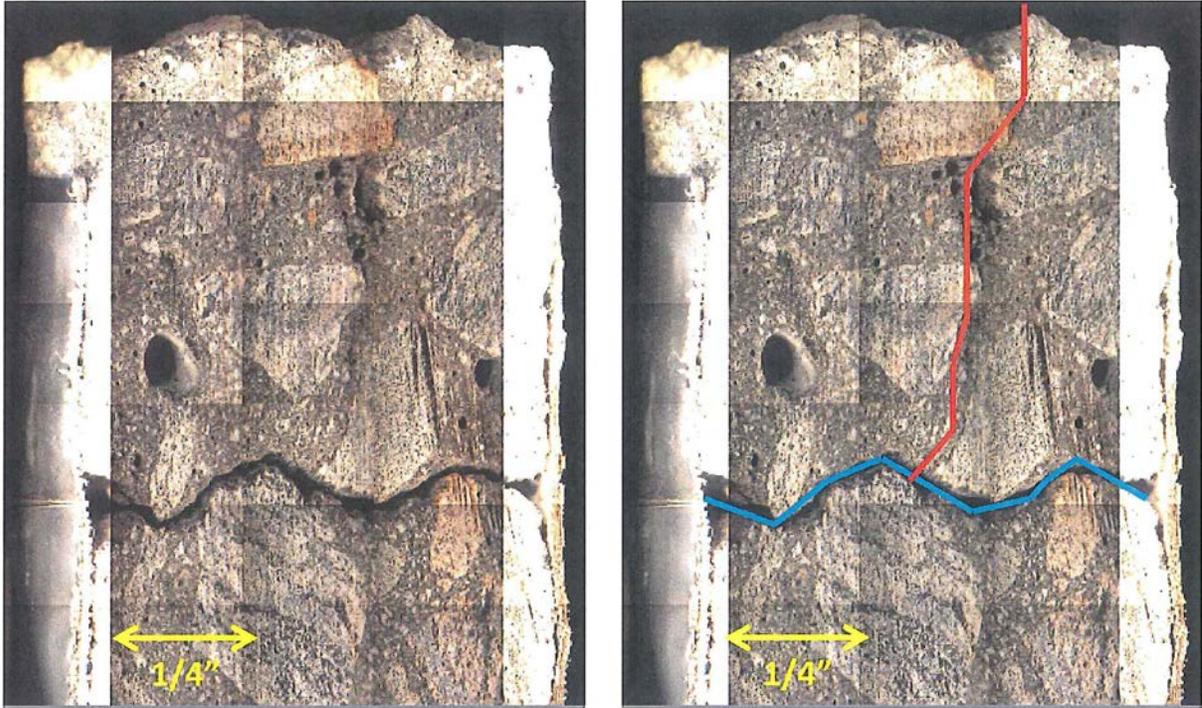


Figure 3.33: concrete core sample. (left) optical image (right) cracks highlighted in optical image

As shown in Figure 3.34, 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).

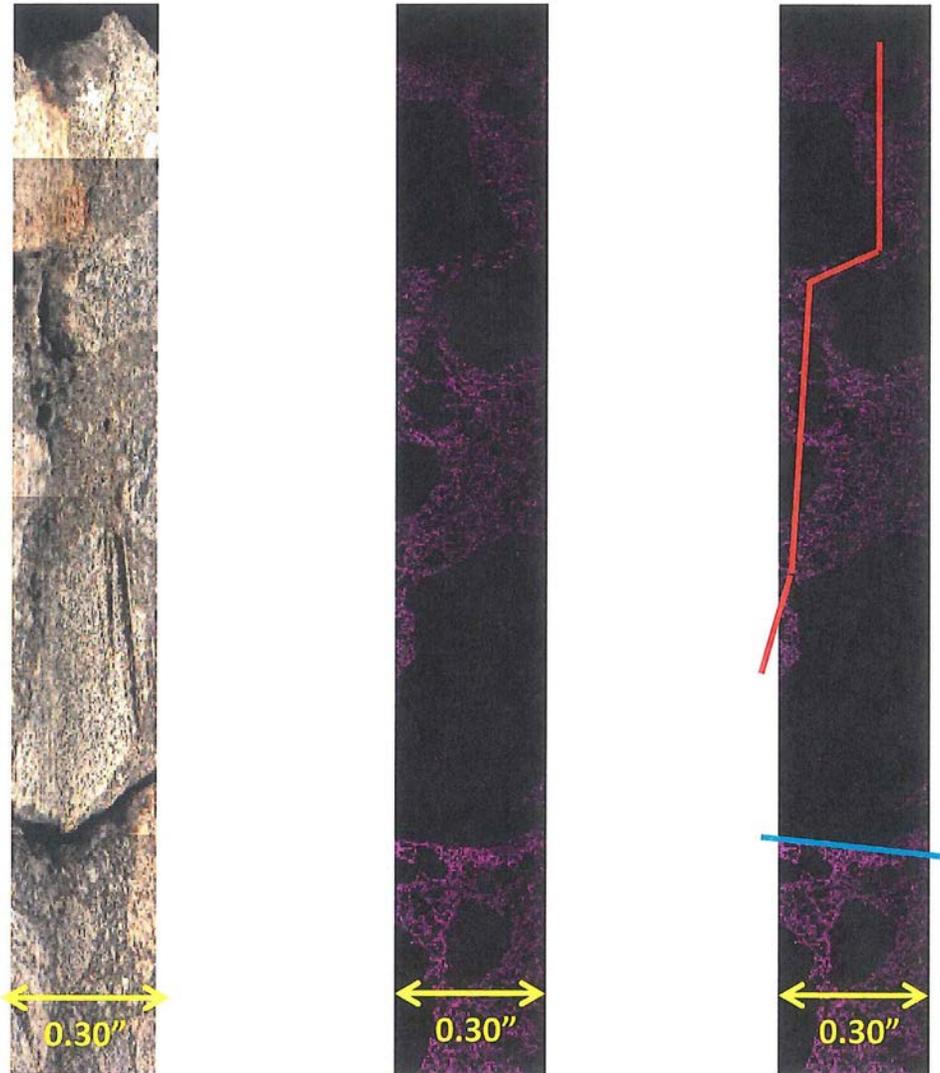


Figure 3.34: concrete core sample (left) optical image (middle) chlorine image (right) cracks highlighted in chlorine image

3.6 Dyes for Selectively Staining Silane or Concrete to Allow Visual Inspection and XRF Mapping

In this work the team developed dyes that selectively dye the silane coating in concrete or the concrete that does not contain the dye so that it can be easily visualized. We found that both neutral red and methyl violet work very well for this purpose. However neither of these dyes was conducive to mapping of the silane coating by XRF microscopy since neither contained elements that were at a high enough concentration to be imaged with the mXRF.

Therefore a range of brominated dyes were used to find one that would selectively stain the silane coating and not the concrete. We found dyes that selectively stained the concrete but not the silane (see below), dyes that stained both silane and concrete, but not one that exclusively dyed the silane, Therefore, we decided to synthesize a dye for this this purpose by using an effective “silane only” dye, methyl violet 2B (Figure 3.35), as the starting material.

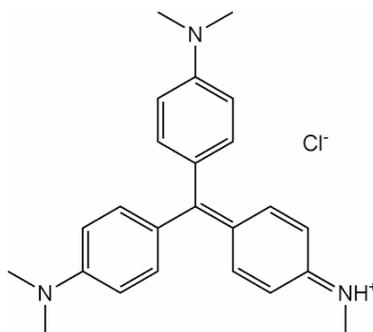


Figure 3.35: A methyl violet 2B molecule

What was desired was a dye with bromine covalently bound to the dye molecules. Therefore, a dye was produced from the reaction of methyl violet with molecular bromine. The methyl violet was first freed from the chloride by adding it to a 1 M sodium hydroxide solution. Under these conditions, the methyl violet precipitated as a black solid that was then filtered and washed with additional 1 M sodium hydroxide solution and then water. The free-based methyl violet was then dried and dissolved in absolute ethanol. Next, a molar equivalent of bromine added drop wise to the ethanol solution with stirring over 20 min. The solution was allowed to evaporate and the resulting solid was collected and dissolved in water and a small amount of insoluble materials was filtered off. The resulting dark blue material was shown to contain bromine by XRF spectroscopy. The dark blue dye was used to dye pieces of concrete that had been treated by silane and the material was found to dye the silane very effectively as is shown on the left in Figure 3.36.

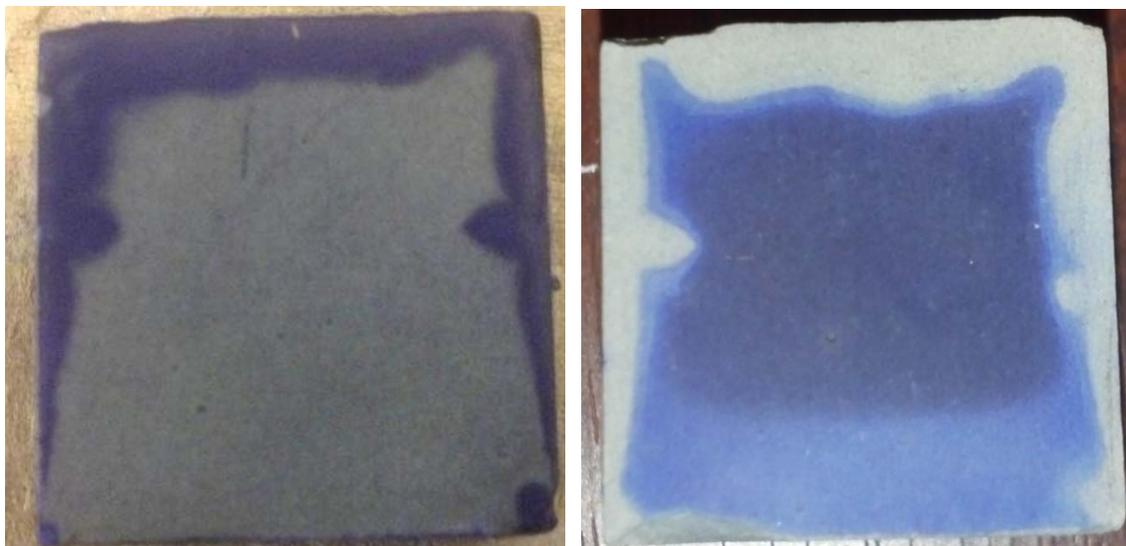


Figure 3.36: (left) brominated methyl violet 2B (right) Bromophenol blue

Figure 3.36. The image on the left shows a cement paste sample that has been treated with silane and then dyed with brominated methyl violet 2B for 1 min. The sample on the right is the other side of the fracture that shows the sample dyed with bromophenol blue for 10 seconds. Note that the images are negatives of one another.

In searching for a brominated dye for selectively staining silanes, it was found that Bromophenol blue could selectively dye concrete but not the silane coating. We had been using a chloride based blue dye for this purpose and then mapping the chlorine with XRF microscopy. However, it is possible that concrete samples already contain significant amounts of chloride. Therefore, we were interested in bromophenol blue as a “negative stain” for the absence of silane. The dye was used as is and found to stain the concrete portion of silane containing samples in as little as 10 sec. Results are shown on the right in Figure 3.36. Cores from concrete structures that had been treated with silane and mapped with the brominated methyl violet dye are shown in Figure 3.37. In the optical image one can see a change in the color of the sample at the interface between the treated and non-treated sections. This same boundary is clearly shown in the μ -XRF.

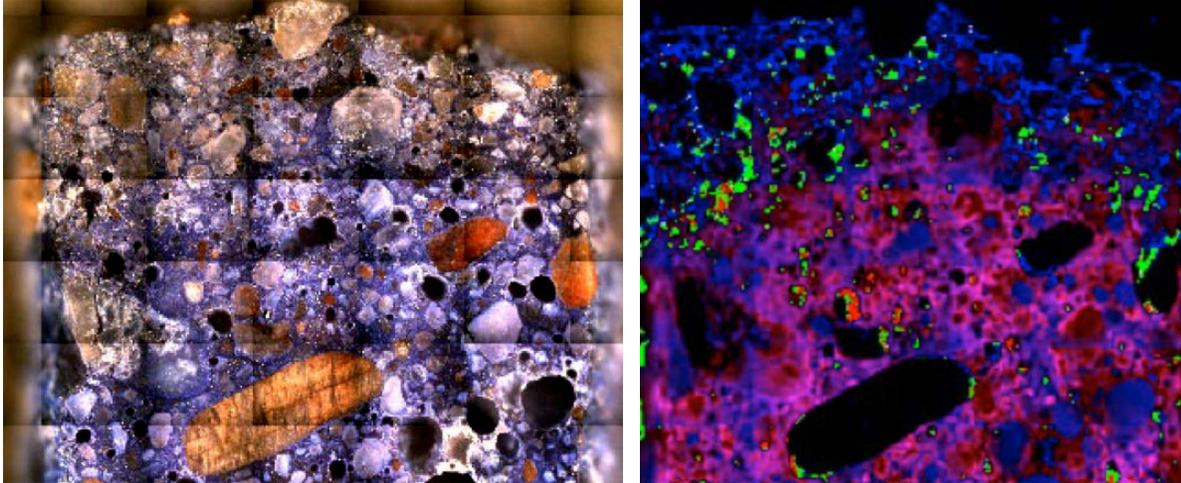


Figure 3.37: (left) optical image of a concrete sample that has been dyed with brominated methyl violet 2B (right) the same area is imaged with the μ -XRF. High bromine concentration is red and pink and lower bromine concentration is blue in this map. The boundary between the pink and blue matches the boundary from the optical images.

3.7 Contact Angle Measurements

The contact angle is a quantitative measure of the wetting of a solid by a liquid. It is defined as the angle formed between the liquid/solid and liquid/vapor interfaces. As the contact angle becomes larger, the surface is becoming more hydrophobic or water resistant. Since silane coatings are water repellent, a good silane coating is expected to give larger contact angles than the untreated concrete. In general, the more attractive the water is to the concrete surface, the smaller the contact angle

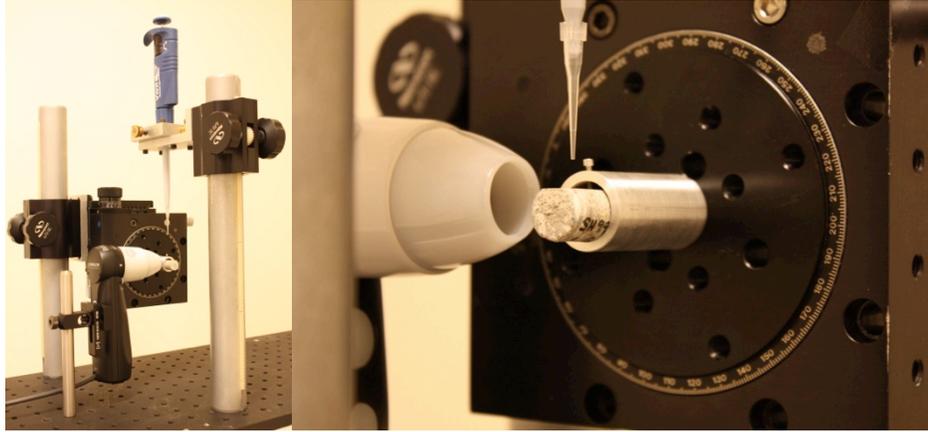


Figure 3.38: Our contact angle measurement device and a close-up of the sample holder. Not shown are the three micrometers that are used for fine positioning of the sample with respect to the camera.

To study the concrete samples, we constructed a surface angle measurement device custom tailored for concrete work, as shown in Figure 3.38. This device utilizes the sessile drop method to measure the contact angle. Our device is comparable to a commercial device except that the sample stage has more degrees of freedom, including sample translation to allow measurement along the length of a concrete core. A micropipette is utilized to create very small droplets on the surface. Using the micropipette, a 1 to 10 μL drop is formed on the end of a flat needle and then transferred the surface by touch. For very small droplets, the creation of a freely falling drop is not possible.



Figure 3.39: Graphical illustration of the contact angle and water droplet on glass.

The left image in Figure 3.39 shows how the angle is defined. For a small droplet, gravity affects the shape resulting in an ellipsoidal appearance. To obtain the angle, a digital camera captures the profile of the liquid droplet on the substrate. The right panel

of Figure 3.39, shows a droplet collected by our system. ImageJ, a public domain Java image processing program inspired by NIH Image, is used to analyze the captured droplet. For computing the contact angle, we use a plug-in, written by Marco Brugnara, to calculate the contact angle of a drop on a flat surface. To test our instrument, our first measurements were performed on round test samples. However, the round samples gave some difficulty in controlling the location of the drop. For the measurements of concrete samples, we utilized samples prepared for μ -XRF experiments. These samples were around ¼” in diameter and polished on one side (see the sample in the right image in Figure 3.38).



Figure 3.40: Positioning of a water droplet on sample SH-51 for contact angle measurements.

For these measurements, a 10 μ L drop was placed in locations dominated by the paste from top to the bottom of the sample (see Figure 3.40). Ten minutes were allowed to pass to ensure that the droplet was stable. We chose 10 μ L as a good compromise for spatial resolution and ease of measurement.

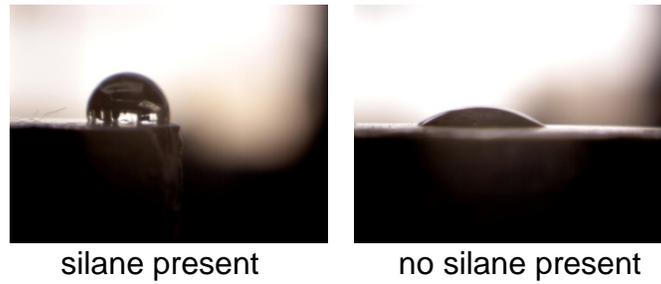


Figure 3.41: Images from the top of a silane treated sample (sample SB-99-2B) and from a location 6 mm into the sample. In this case there is a clear difference in the contact angle measurement.

Figure 3.41 shows two images collected from a silane treated bridge deck. The first image is for a droplet placed at top of the sample while the other is from an innermost section of the sample. The droplet in the left image is clearly more spherical than the right one. Clearly the contact angle for the silane treated section is much larger than that for the untreated material. All images were fit using an elliptical function to the outline of the droplets. The elliptical fitting corrects for gravity, which tends to flatten the droplet. In addition, the fitting takes into account the complete profile and corrects for any bulging, optical distortions or any other imperfections at the interface that can reduce the apparent angle determined by a simple tangent line.

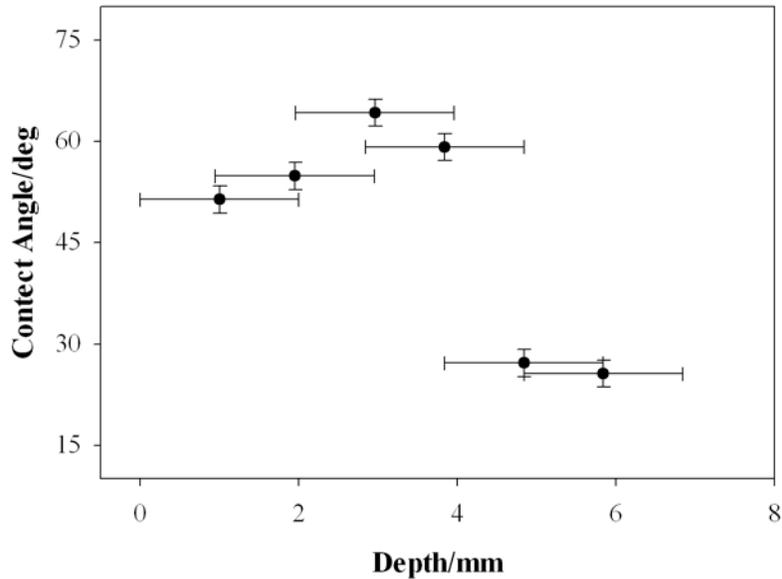


Figure 3.42: Contact angle measurement versus depth for SH-99-2A sample. SH-99-2B was very similar. The x error bars represent the drop size and the y error bars represent an assigned uncertainty based on multiple measurements.

In general, two different results were obtained by the contact measurement. Figure 3.42 shows the results for the SB-99-2A sample. In this figure, the x error bars represent the drop size and the y error bars represent an assigned uncertainty based on multiple measurements. For each sample at least two measurements were made at each depth. The small increase for this sample at around 3 mm is repeatable over multiple measurements. For the SB-99-2B sample, the surface contact measurement is abnormally high, possible due to the presence of oil or other material on the surface.

Table 3.7: Average surface and internal contact angle measurements and crossover point. Sample SH-51 had a very small, yet detectable, change in the contact angle.

Sample	Surface/deg	Internal/deg	Crossover Depth/mm
SH-99-2A	57 ⁰	26 ⁰	4.5
SH-99-2B	67 ⁰	36 ⁰	6
SH-3	51 ⁰	36 ⁰	4
SH-51 #1	70 ⁰	48 ⁰	3.5
SH-51 #2	63 ⁰	59 ⁰	2

For the different samples, the results are summarized in Table 3.7. The crossover point is the distance where the surface contact angle drops to a value close to that for the material deep within the sample, or the internal contact angle. The reported internal contact angle is an average of the data points below the crossover depth to the deepest point measured. The contact angles for the siloxane treated surface were all greater than about 60°. For the first three samples the internal contact angle was consistently small. For the SH-51 sample the contact angle within the concrete was significantly larger than the first three, something to be further investigated.

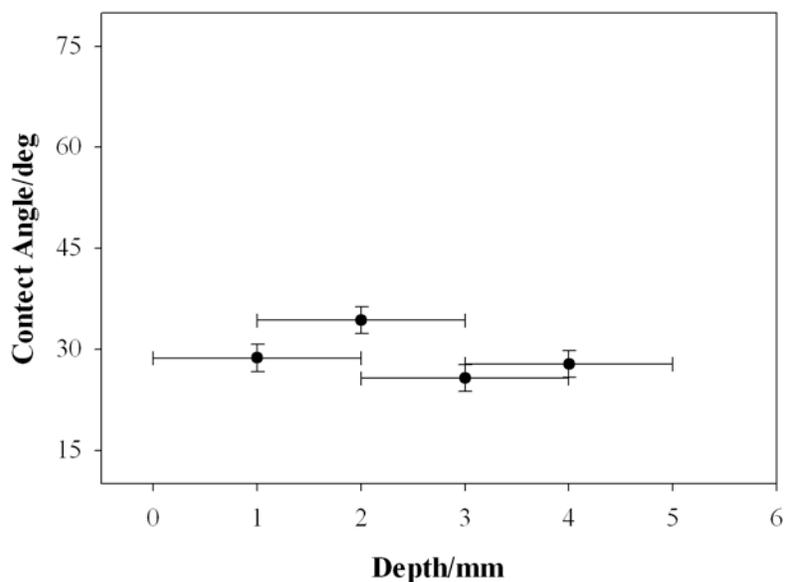


Figure 3.43: Contact angle measurement versus depth for I-40 sample.

For the I-40 sample, shown in Figure 3.43, the contact angle is essentially unchanged with depth. Either there was no siloxane coating or it has completely deteriorated. The average contact angles for the other sample, which showed little variation in angle with depth, are shown in Table 3.8.

Table 3.8: Average contact angles for samples without a clear crossover point.

Sample	Contact Angle/deg
I-40	29°
US-62 #1	35°
US-62 #2	31°

In general, the contact angles for the siloxane treated surface were typically greater than about 60°. The internal contact angles were consistently smaller, generally less than around 35° or half of that from the siloxane treated surface. For the SH-51

samples the contact angle within the concrete was significantly larger than all other samples, something to further investigated.

3.8 XPS Measurements

X-ray photoelectron spectroscopy (XPS) is a quantitative spectroscopic technique that measures the elemental composition and the electronic state of elements on the surface of a material. For these experiments, XPS is used to measure the binding energy or the energy in which the silicon atoms in the sample hold the 2p electron. Silicon oxide, such as quartz, will have a higher binding energy than the silicon atoms in the siloxane material. The XPS measurements are performed using the Mg anode of a PHI 300 Watt Twin Anode X-ray source. A PHI double-pass cylindrical mirror analyzer with a pass-energy of 50 eV detects the resulting photoelectrons. Since the samples are non-conducting, the energy scale was corrected using the carbon 1s binding energy as a standard.

The sampling area is approximately 1 mm² and the top measurement is centered approximately 1.5 mm from the surface. Each measurement is taken in approximately 1.5 mm increments. Therefore the second measurement is approximately 3 mm from the surface and so on. However, these numbers are obtained from the manufacture and have not been independently verified. For the I-40 and other samples, which have little variation in contact angle, very little change in the silicon 2p spectra is noticed (left panel in Figure 3.44). For the sample in which a silane coating is detected using contact angle measurement, a slight shift to lower energy is observed. Further experimentation and fitting the area under the curves is required to confirm and understand these results. However, it is possible that the silica oxide background is too high to obtain clear results.

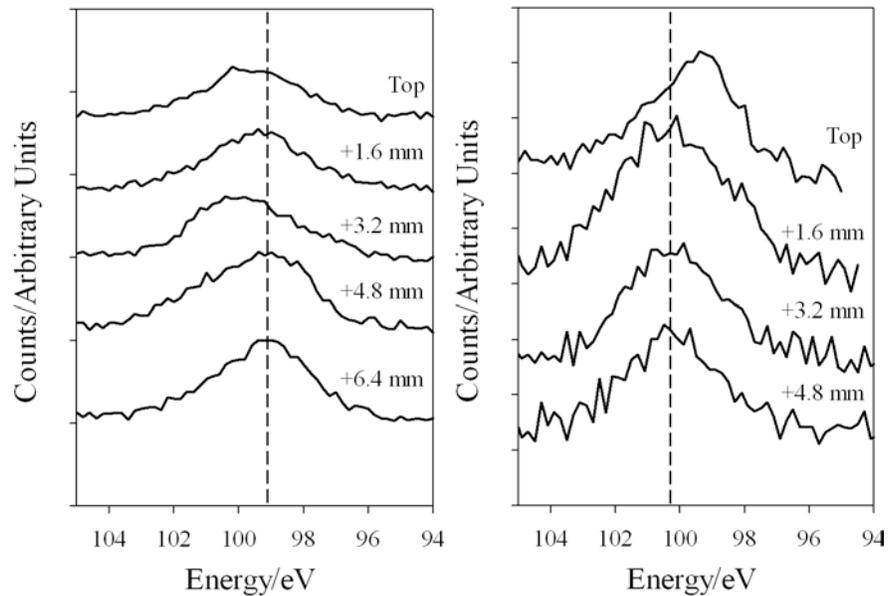


Figure 3.44: Left is the Si 2p XPS spectrum for the I-40 sample while the right is the Si 2p XPS spectrum for the SH-99-2A sample. All spectra were reference to the carbon 1s binding energy. These are the same samples that the contact angle measurements were performed on (Figures 3.43 and 3.42).

Chapter 4: Using Non-Destructive Field Testing Techniques to Find 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 to be tested in the laboratory. The purpose of this testing was to provide information on how long silane treatments last. Second, field testing techniques were used in order to confirm the presence of the silane treatment.

4.2 Core Samples

In order to determine how long silane treatments last, 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 4.1. Whenever possible, cores were also taken from the travel lane in order to examine the effects of erosion on the silane treatment.



Figure 4.1: (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 4.2.

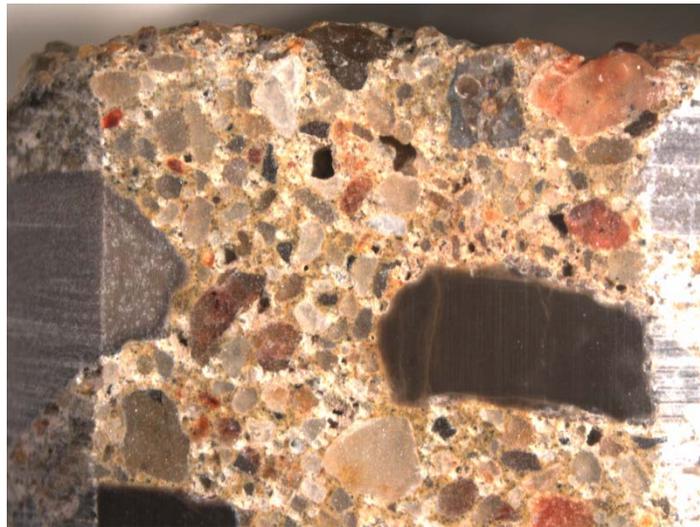


Figure 4.2: Example of a core sample that has been polished

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



Figure 4.3: Example of a core that was ponded 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 4.4. 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.

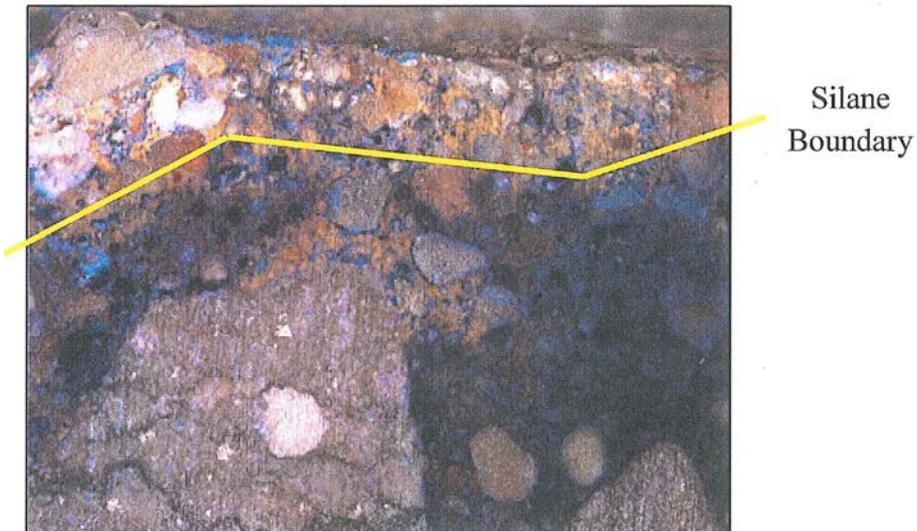


Figure 4.4: Example of a core that was ponded in a chloride-based dye

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 4.4, 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 4.5, two 12" x 12" x 2" specimens were cast and allowed to cure for about a week before testing.



Figure 4.5: 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. 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 4.6, to mark where measurements would be taken with the Wenner probe.

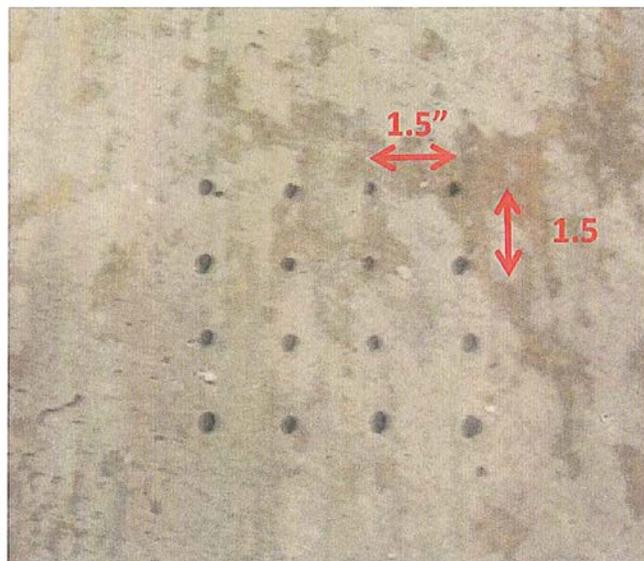


Figure 4.6: example of a grid placed on the formed side of a specimen

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 4.7, 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 4.7: 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 Figures 4.8. By comparing the results in Figures 4.8, 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.

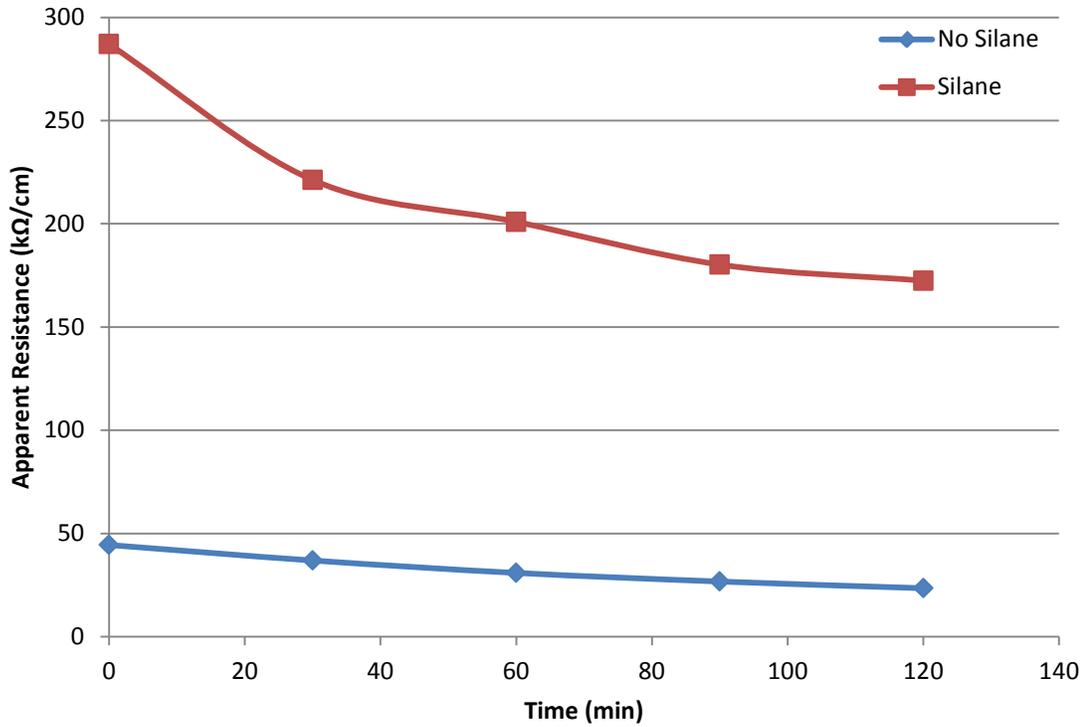


Figure 4.8: comparison of average resistance vs time between specimens treated with silane and specimens not treated with silane

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 4.9. 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 4.9: 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 4.10, 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 4.10: 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 4.11.

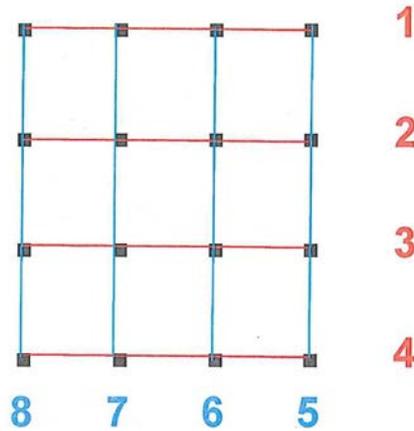


Figure 4.11: Example of taking measurements

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 4.12. Measurements were taken in the same manner described in Figure 4.11.



Figure 4.12: 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 4.13. 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 4.14. Next, the columns were filled with water past the seal and allowed to pond for 30 minutes.



Figure 4.13: Example of a water column setup



Figure 4.14: 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 4.11.

As shown by the example in Figure 4.15, all measurements were plotted and compared. Figure 4.15 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).

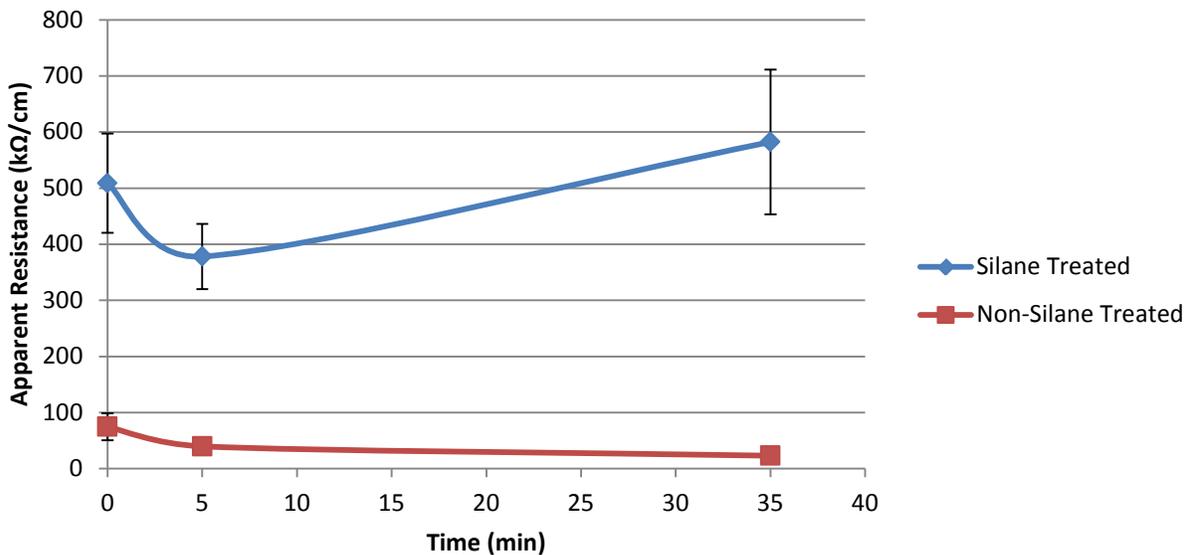


Figure 4.15: Example of a comparison between a bridge deck that shows evidence of silane (SH-18 #1 Grid #3) and a bridge that does not (US-75 Grid #1)

There is a difference of approximately one order of magnitude between that which shows evidence of a silane treatment and that which does not.

4.4 Conclusion

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

Chapter 5: Investigation of the Presence of Silane in Concrete Using Field and Laboratory Techniques

5.1 Overview

Various field and laboratory techniques were employed to investigate the presence and effective lifespan 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 (μ -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 "diam x 1" height) were taken from each bridge deck and tested using the brominated dye, chlorine based dye, and μ -XRF. Ponding times for the brominated and chlorine based dyes were 30 seconds and 30 minutes, respectively.

5.2 Results

Table 5.1 summarizes the results of the determination of the presence of silane using all three techniques. Table 5.2 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 5.1: 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 (μ -XRF)	Chlorine Image (μ -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	<u>N</u>	Y	-	-
	-97° 36' 48.5"		Travel Lane	-	N	Y	-	-
SH33	35° 52' 16.5"	6	Shoulder	Y	N	<u>N</u>	-	-
	-97° 36' 21.6"		Travel Lane	-	**	**	-	-
SH33	35° 59' 18.6"	10	Shoulder	Y	N	Y	-	-
	-96° 17' 07.4"		Travel Lane	-	<u>N</u>	Y	-	-
SH33	35° 57' 05.9"	9	Shoulder	Y	N	Y	-	-
	-97° 16' 09.0"		Travel Lane	-	N	<u>N</u>	-	-
SH33	35° 57' 07.1"	9	Shoulder	Y	Y	<u>N</u>	-	-
	-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	<u>N</u>	-	-
	-97° 04' 09.1"		Travel Lane	-	**	**	-	-
SH51	36° 06' 96.0"	Not Treated	Shoulder	Y	N	<u>N</u>	-	-
	-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	<u>N</u>	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 /	35° 34' 31.8"	6	Shoulder	Y	N	Y	-	-

SH99	-96° 39' 48.6"		Travel Lane	-	N	Y	-	-
US377 / SH99	35° 41' 06.3"	6	Shoulder	Y	N	<u>N</u>	-	-
	-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) and the test was unable to be performed.**

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

Table 5.2: 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"	6	Shoulder	N	-
	-96° 53' 17.1"		Travel Lane	***	-
SH18	35° 38' 52.2"	6	Shoulder	Y	1/8
	-96° 53' 16.2"		Travel Lane	Y	1/8
SH33	35° 57' 57.5"	7	Shoulder	**	-
	-97° 14' 02.4"		Travel Lane	**	-
SH33	35° 52' 16.5"	6	Shoulder	Y	1/8
	-97° 36' 48.5"		Travel Lane	Y	1/16
SH33	35° 52' 16.5"	6	Shoulder	<u>N</u>	-
	-97° 36' 21.6"		Travel Lane	**	-
SH33	35° 59' 18.6"	10	Shoulder	Y	1/8
	-96° 17' 07.4"		Travel Lane	Y	¼

SH33	35° 57' 05.9"	9	Shoulder	Y	1/8
	-97° 16' 09.0"		Travel Lane	<u>N</u>	-
SH33	35° 57' 07.1"	9	Shoulder	<u>N</u>	-
	-97° 16' 09.1"		Travel Lane	N	-
SH51	36° 06' 57.0"	5	Shoulder	Y	1/8
	-97° 06' 08.0"		Travel Lane	Y	1/16
SH51	36° 06' 56.8"	5	Shoulder	Y	1/16
	-97° 05' 57.0"		Travel Lane	Y	1/16
SH51	36° 07' 39.1"	Not Treated	Shoulder	<u>N</u>	-
	-97° 04' 09.1"		Travel Lane	**	-
SH51	36° 06' 96.0"	Not Treated	Shoulder	<u>N</u>	-
	-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	<u>N</u>	-
	-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) 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 4.16.

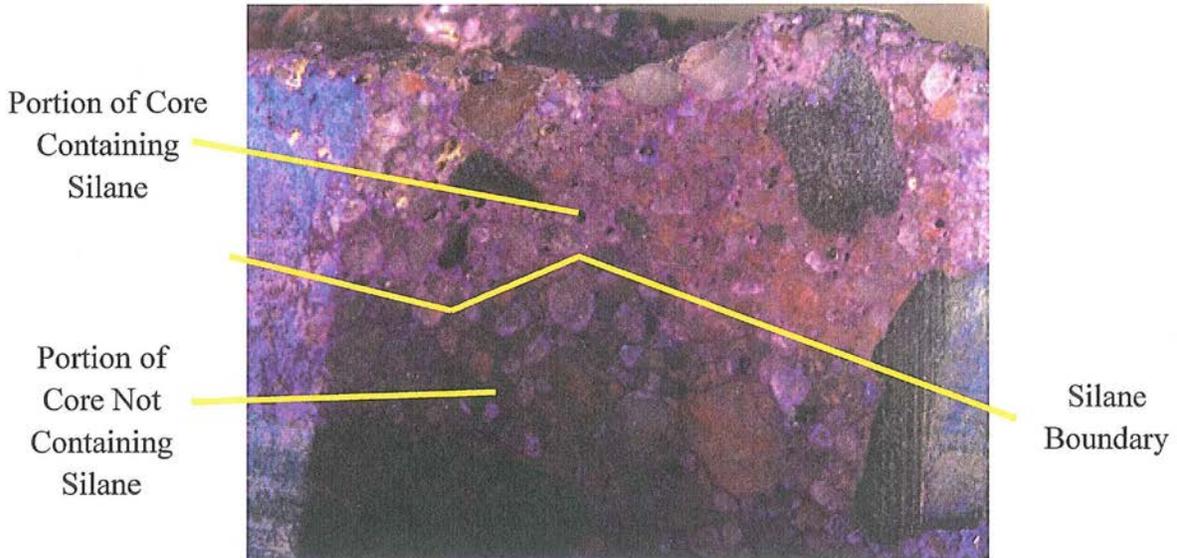


Figure 4.16: example of brominated dye staining both portions of the concrete sample

Since the Wenner Probe and the brominated dyes posed these issues and the μ -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 5.3 summarizes this data.

Table 5.3: Summary of Data from Chlorine-Based Dye

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

As shown in Table 5.4, the useful lifespan of silane on concrete bridge decks in the state of Oklahoma is summarized.

Table 5.4: Summary of Useful Lifespan of Silane Treatment

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

5.4 Recommendations and Discussion

From Table 5.4, it was concluded that the useful lifespan of a silane treatment on a concrete bridge deck is 5-6 years. Table 5.4 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.

Chapter 6: Determining the Ability to Reapply Silane in Field Concrete

6.1 Overview

In Chapter 5, testing to determine the presence and effective lifespan of silane in field concrete was discussed. This testing was conducted on core samples (approximately 0.5" dia. x 1" height) that were taken from various bridge decks in the state of Oklahoma. After completing this testing, the cores were further tested to determine the ability to reapply silane to this concrete.

6.2 Laboratory Testing

In order to determine whether or not silane can be reapplied to concrete surfaces, cores were taken from bridges in the state of Oklahoma, where the treatments had an age range of 5-10 years, and subject to a series of laboratory testing.

21 cores from 12 different bridges, with treatment ages ranging from 5-8 years were polished through the depth to establish a flat surface as shown in Figure 6.1.

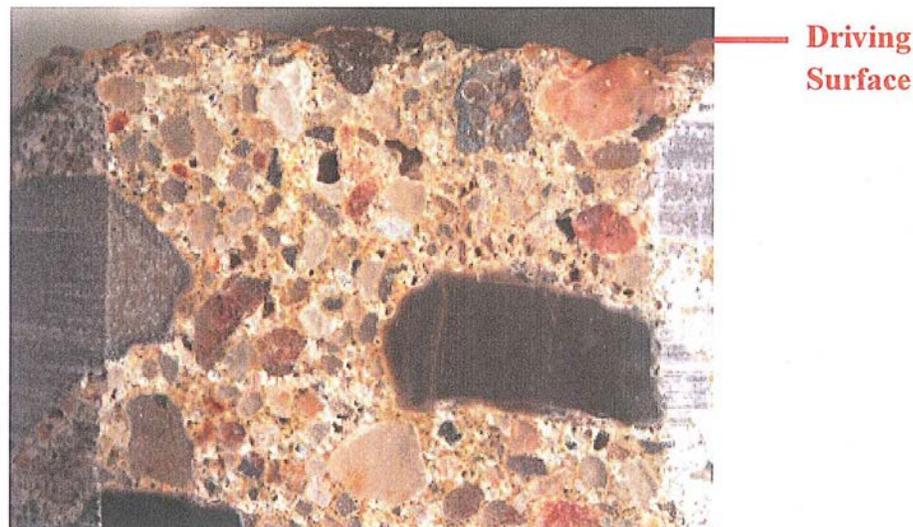


Figure 6.1: Example of a core that has been polished

After polishing, all faces of each core except the finished surface was thoroughly coated with wax. Next each core was completely submerged in silane and allowed to pond for 20 minutes, as shown in Figure 6.2, because in prior testing it was found that a ponding

time of 20 minutes was required in order for silane to penetrate a concrete sample to a depth of 1/8".

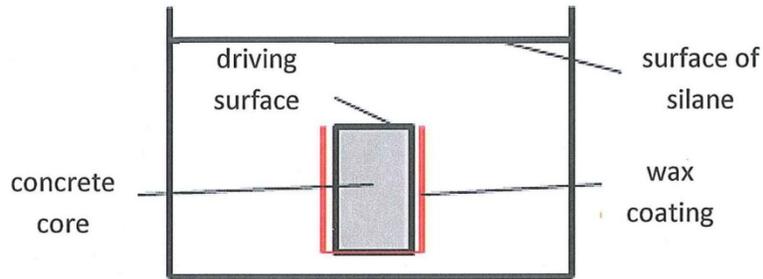


Figure 6.2: Test setup for ponding concrete cores in silane

After ponding each core was allowed to dry for at least 30 minutes. The wax was then removed from the previously polished surface and each core was ponded for 30 minutes in a chlorine-based colored dye in the same manner described in Figure 6.2. The colored dye established a visual contrast by staining all concrete in the core that was untreated with silane, as shown in Figure 6.3.

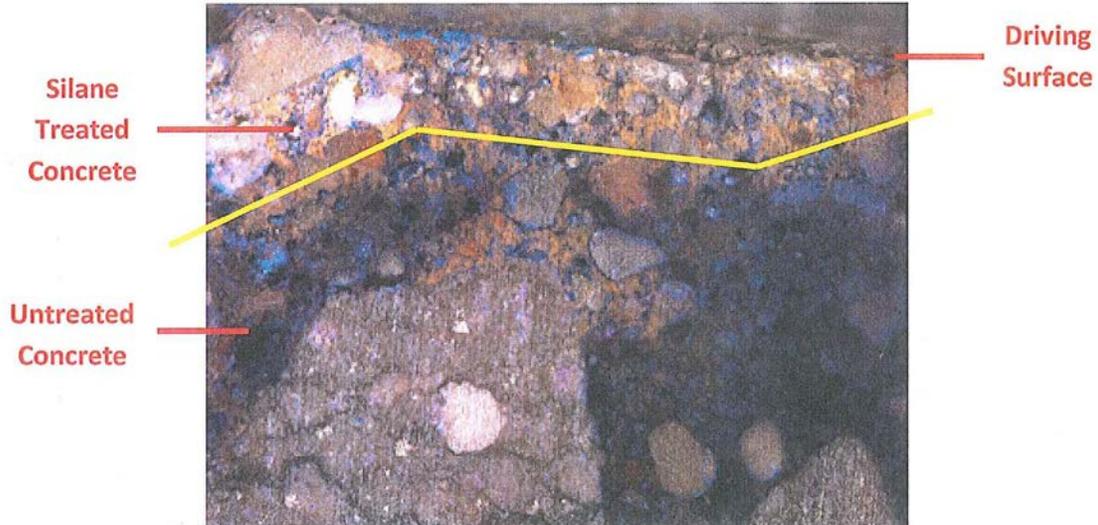


Figure 6.3: Example of a core that has been ponded in the chlorine-based colored dye

The process was then repeated a second time for each core (i.e. a total of 40 minutes of ponding in silane), where the cores were polished a second time before ponding in the colored dye to expose a fresh surface.

6.3 Results

Table 6.1 summarizes the results of the laboratory testing performed to determine if silane can be reapplied to concrete surfaces. Table 6.2 summarizes the percentage of samples that showed improvement in the depth of penetration after reapplication of silane.

Table 6.1: Results of reapplying silane to concrete core samples

Roadway	Years of Service	Location	Total Depth (in) at Ponding Time X			Did Depth of Penetration Improve After Time X?	
			0 Min	20 Min	40 Min	20 Min	40 Min
SH-51 (Stillwater Creek)	5	Shoulder	1/8	3/16	0	Yes	No
		Travel Lane	1/16	1/8	1/8	Yes	Yes
SH-51 (Cow Creek)	5	Shoulder	0	0	3/16	No	Yes
		Travel Lane	1/16	0	1/16	No	No
US-75 (Childers Creek)	5	Shoulder	1/16	0	1/4	No	Yes
		Travel Lane	3/16	0	5/16	No	Yes
SH-18	6	Shoulder	0	1/2	1/4	Yes	Yes
		Travel Lane	-	-	-	-	-
SH-18 (Deep Fork River)	6	Shoulder	1/8	1/8	1/8	No	No
		Travel Lane	1/8	0	3/16	No	Yes
SH-33 (Pawnee Creek)	6	Shoulder	1/8	1/16	0	No	No
		Travel Lane	1/8	0	1/8	No	No
SH-33 (Cox Creek)	6	Shoulder	0	1/16	0	Yes	No
		Travel Lane	-	-	-	-	-
US-377 #1 (Deer Creek)	6	Shoulder	0	3/16	1/4	Yes	Yes
		Travel Lane	-	-	-	-	-
US-377 #2 (Deer Creek)	6	Shoulder	1/8	0	5/16	No	Yes
		Travel Lane	1/16	0	0	No	No
US-377 #3	6	Shoulder	1/16	1/8	3/16	Yes	Yes
		Travel	1/8	1/4	1/4	Yes	Yes

		Lane					
US-377 #4	6	Shoulder	1/8	3/16	3/16	Yes	Yes
		Travel Lane	1/8	3/16	3/8	Yes	Yes
US-75 (Duck Creek)	8	Shoulder	1/4	0	0	No	No
		Travel Lane	1/4	0	0	No	No
SH-51 (Mehan Road)	8	Shoulder	1/8	0	3/8	No	Yes
		Travel Lane	-	-	-	-	-
SH-51 (Cimarron River)	9	Shoulder	1/8	1/8	3/16	No	Yes
		Travel Lane	1/16	1/8	1/8	Yes	No
SH-51 (Cimarron Overflow)	9	Shoulder	0	0	0	No	No
		Travel Lane	0	-	-	-	-
SH-33 (Fitzgerald Creek EB)	9	Shoulder	0	0	0	No	No
		Travel Lane	1/8	0	0	No	No
SH-33 (Fitzgerald Creek WB)	9	Shoulder	0	1/4	5/16	Yes	Yes
		Travel Lane	0	0	0	No	No
SH-99 (Hominy Creek)	10	Shoulder	1/8	0	1/4	No	Yes
		Travel Lane	1/8	3/16	3/16	Yes	No
SH-33 (Tiger Creek)	10	Shoulder	0	3/16	5/16	Yes	Yes
		Travel Lane	1/4	0	3/16	No	No

Table 6.2: Summary of Depth of Penetration Improvement After Reapplication

Age	Total Cores Tested	% Improved After 20 Min	% Improved After Either 20 or 40 Min
5	6	33.3	83.3
6	13	53.9	69.2
8	3	0.0	33.3
9	7	28.6	42.9
10	4	50.0	75.0

6.4 Discussion and Recommendations

Based upon the results shown in Tables 6.1 and 6.2 it was challenging to reapply silane after the structures had been in service for more than six years. Furthermore, it was

typical for this reapplication to take increased soak periods for the silane to penetrate into the samples. This suggests that when silane is reapplied in the field that it may take increased efforts. It should be noted that the techniques used in this study were only done with lab testing and furthermore, did not use a technique that even simulated the spray application of silane in the field. However, this technique still does provide a useful comparison of the ease at which silane can be re-applied in mature concrete.

It was not possible to investigate how long this reapplied silane will last, and if it is possible for silane to continue to be reapplied. This is an area for future research.

One possible cause for silane not being able to create a hydrophobic layer in the concrete could be the presence of debris in the pores or perhaps localized surface carbonation that may make it difficult for the silane to bond to the surface. It is also possible that the original coating is present and does not allow for reapplication. It should also be noted that all measurements were taken within a day of ponding of the silane application. Discussions with silane vendors suggest that the material may continue to penetrate over time. This was not investigated with this testing and is another area of future research. It is suggested that care be taken to examine the effectiveness of reapplying silane on existing structures and that additional efforts may be needed to either prepare the surface or multiple coats of material.

Chapter 7: Summary

This section provides a summary of the work in this report. A thorough literature review on silane and applications as a concrete sealer has been provided. Several laboratory and field based tests were investigated. The research has found that the GWT was not useful but the four point Wenner probe showed potential for both laboratory and field concrete. Several novel dying techniques were presented, along with a method to measure the contact angle of water with the samples.

After investigating field concretes it was found that the chloride based dye was the best method to reliably stain concrete that did not have silane present. This allowed for an easy visual inspection to be made between the material with and without silane. By using this technique it was found that the useful lifespan of a silane treatment on a concrete bridge deck is reliably 5 to 6 years for the bridges investigated.

When investigating the reapplication of silane to concrete samples it was found that it would be best if silane should be reapplied to concrete surfaces within the first 6 years after the first treatment. This reapplication will likely require more effort than what is required to get 1/8" penetration in young concrete. It should also be noted that as the concrete increased in age that the probability decreased that the silane could be reapplied. More work is needed to investigate actual field performance of silane reapplication.

The information presented can be used by DOTs to better understand the effective life of a silane sealer and the ability for this material to be reapplied over the life of the structure. This can help in the long term maintenance decisions of their structures.

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