Expected Life of Silane Water Repellant Treatments on Bridge Decks

ANNUAL REPORT FOR FY 2011
ODOT SPR ITEM NUMBER 2229

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October, 2011

CHAPTER I

INTRODUCTION

The Oklahoma Department of Transportation (ODOT) commonly uses a silane chemical sealer on new bridge decks to reduce the penetration of external chemicals and help extend the life of the bridge. Currently, it is unknown how long these sealers are effective, and if these sealers can be reapplied to existing concrete after the silane has stopped performing.

In this project the research team will evaluate the effectiveness of silane coatings of bridge decks at different ages through laboratory and non-destructive field techniques to determine their effective life. Methods to reapply the silanes to mature concrete will also be investigated.

The tasks for this project are:

1. Literature Review
2. Establish Laboratory Procedures to Evaluate Silane Performance
3. Investigate Non-Destructive Field Techniques to Evaluate Silane Performance
4. Determine the Effectiveness of Silanes for In-Service Bridge Decks
5. Investigate Methods of Reapplication of the Silanes to Mature Concrete
6. Final Report

This project will establish a non-destructive technique to evaluate the effectiveness of silane sealers. This technique will allow ODOT to make informed maintenance decisions about when and how to reapplying silanes to bridge decks. The successful long term usage of silanes will help minimize the penetration of outside chemicals into the concrete and help prolong the life of Oklahoma bridge decks. In addition testing would be completed to determine the best methods to reapply silane coatings to bridge decks after they have reached their service life.

CHAPTER II

PROGRESS REVIEW

In this section progress will be given on each of the tasks. Emphasis will be placed on the progress made.

Task I – Literature Review

The research team has looked extensively over the important references on the durability of silane coatings in concrete. From this investigation very little data has been found. However a summary of the findings of this work will be prepared and presented in the final report.

Task II - Establish Laboratory Procedures to Evaluate Silane Performance

The goal of this task is to establish laboratory procedures to evaluate the existence and effectiveness of silane in concrete. After these methods are established they will then be used to evaluate cores from bridge decks taken from the field. The following techniques are being investigated:
1. XRF microscope investigation,
2. contact angle measurements,
3. XPS measurements, and
4. selective silane staining.

XRF Microscope Investigations

Micro X-ray Fluorescence (µXRF) is a 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. The sample will absorb the X-rays and emit a secondary fluoresced X-ray. The fluoresced X-ray intensities are then assigned as pixels into an image. Each element will emit a unique signal allowing individual element images to be produced, like those shown in Figure 1.
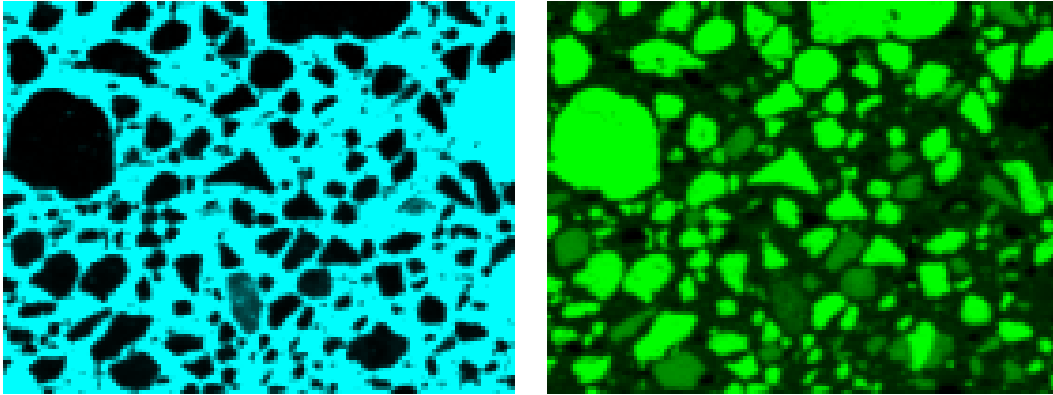
**Figure 1: (left) calcium image (right) silicon image**

Cluster Analysis

The data from the µXRF machine is 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 (which is called a 'phase' by the image processing software). This analysis provides valuable information such as what the sample consists of (i.e. chemical composition), where these components are located on the sample surface, and the quantity of those components at that location.

Clusters, or phases, are developed by selecting areas of high concentration because this is what is most prevalent in any given area. Since an area will most likely consist of multiple elements, the phase will consist of the area of overlap of all elements in consideration for the given phase, as shown in Figure 2.
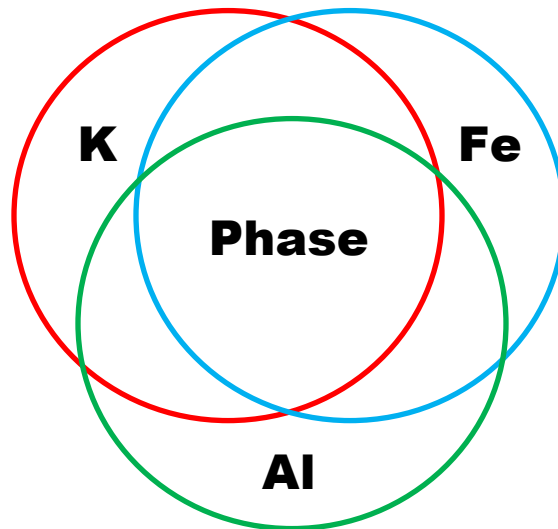

Figure 2: A phase defined by aluminum, iron, and potassium

This process is repeated until the entire surface has been defined (i.e. multiple phases). Then a phase map, like that shown in Figure 3, is produced which combines all individual phases into a single image where each color in the phase map represents a separate phase.
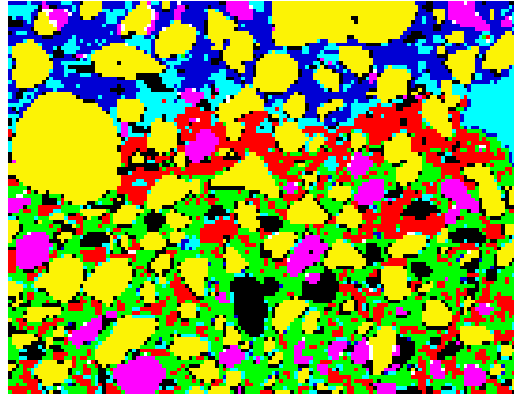

Figure 3: example of a phase map

To investigate the presence of silane a series of scans of silane coated concrete were performed using the machine. The first scan was performed on a coated sample made in the laboratory which was not modified in any way in order to see what kind of data it would produce. One very distinct observation, as shown in Figure 4, was a noticeable high band of sulfur (i.e. bright blue pixels) which was not found in samples without a silane coating. This high band of sulfur was thought to be just below the silane boundary.

5 mm
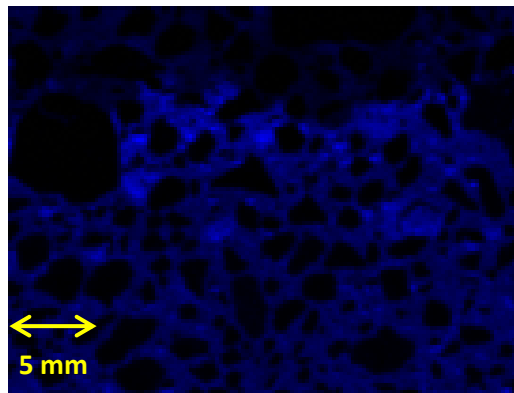
Figure 4: sulfur image from the μXRF machine

To confirm this observation, the sample was ponded in a colored dye for 5 minutes and rescanned. The dye would permeate the concrete only where silane was not present, thus establishing a visual boundary that could be observed. A comparison of an optical image of the sample after it was ponded in colored dye and the sulfur image is shown in Figure 5. The silane boundary has been highlighted with a yellow line.
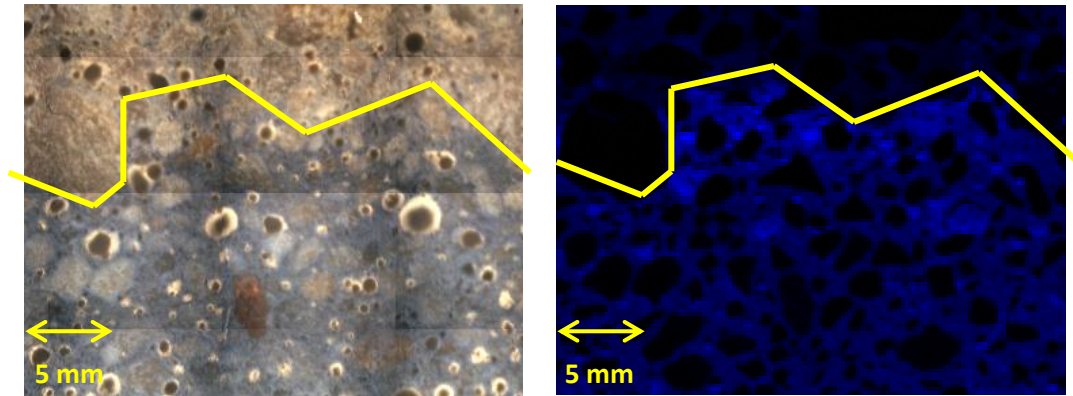
Figure 5: comparison of (left) optical image with colored dye and (right) sufur image

The corresponding phase map is displayed in Figure 6 where the high sulfur band in the cement paste is characterized by the area in red. Likewise, low and medium concentrations of sulfur containing cement paste are characterized by blue and green, respectively. The same boundary that is highlighted by the yellow line in Figure 5 has been highlighted by the black line in Figure 6.
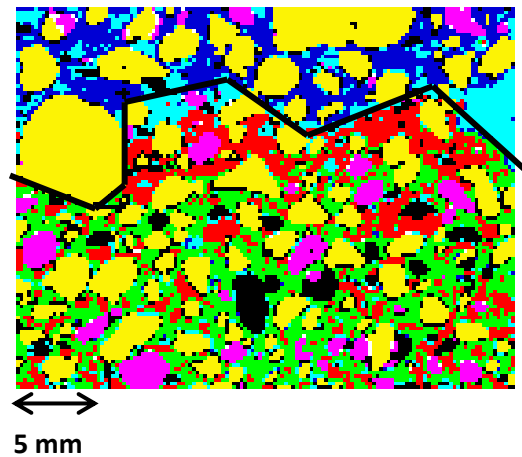
Figure 6: Corresponding phase map

Testing is underway to determine why this band of sulfur is present. This technique has already been used to investigate all of the cores collected from the field.

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
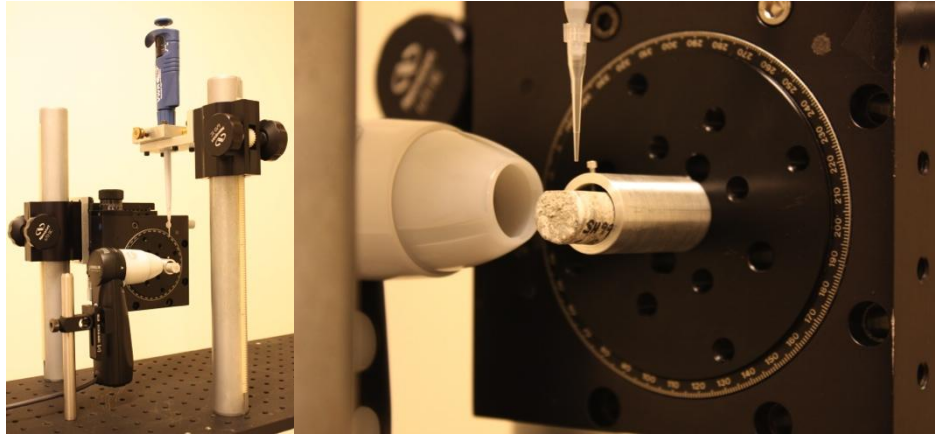

Figure 7: Our contact angle measurement device and a close-up of the sample holder. Not shown are the three micrometers that are used for fine positioning of the sample with respect to the camera.

To study the concrete samples, we constructed a surface angle measurement device custom tailored for concrete work, as shown in Figure 7. 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 8: Graphical illustration of the contact angle and water droplet on glass.

The leftmost image in Figure 8 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 rightmost panel of Figure 8, 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 taken from the bridges, we utilized samples prepared for XRF experiments. These samples were cut with a quarter inch diamond saw and are flat on one side (see the sample in the rightmost image in Figure 7).
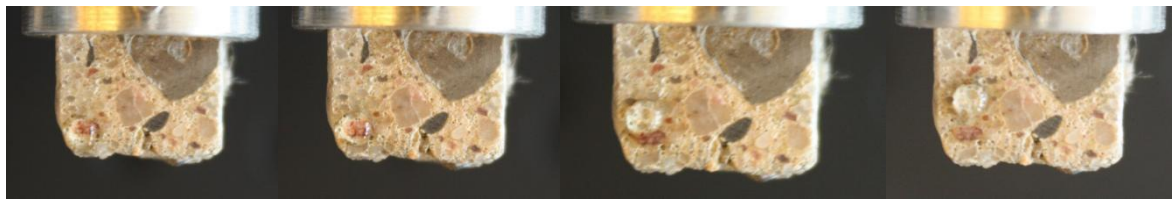

Figure 9: Positioning of a water droplet on sample SH-51 for contact angle measurements.

For these measurements, a 10 μL drop was placed in locations dominated by the paste from top to the bottom of the sample (see Figure 9). Ten minutes were allowed to pass to ensure that the droplet was stable. We choose 10 μL as a good compromise for spatial resolution and ease of measurement.
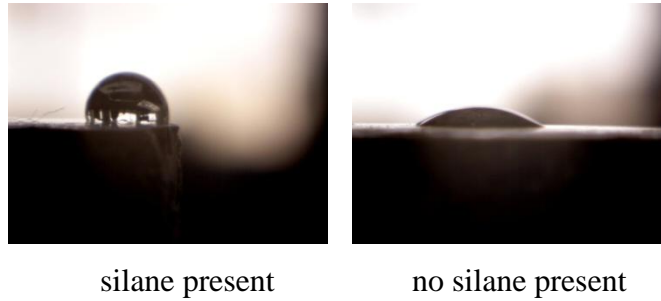
silane present   no silane present

Figure 10: Images from the top of a siloxane treated sample (sample SB-99-2B) and from a location 6 mm into the sample. In this case, the difference is clear, even before data processing.

Figure 10 shows two images collected from a siloxane 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 leftmost image is clearly more spherical than the rightmost one. Clearly the contact angle for the silane treated section is much larger than that for the untreated material deeper within the sample. 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.
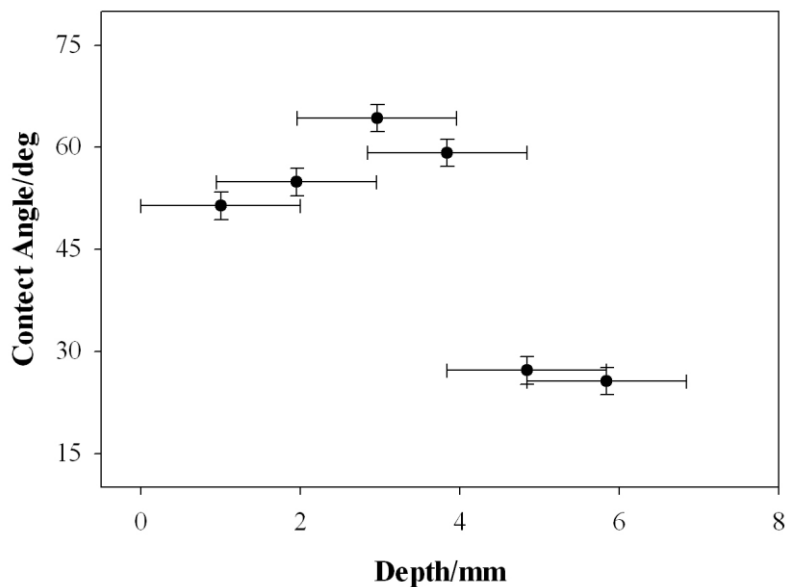
Figure 11: Contact angle measurement versus depth for SH-99-2A sample. SH-99-2B was very similar. The x error bars represent the drop size and the y error bars represent an assigned uncertainty based on multiple measurements.

In general, two different results were obtained by the contact measurement. Figure 11 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. The surface will be further examined after the XRF measurements are preformed.

Table 1: 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°	26°	4.5
SH-99-2B	67°	36°	6
SH-3	51°	36°	4
SH-51 #1	70°	48°	3.5
SH-51 #2	63°	59°	2

For the different samples, the results are summarized in Table 1. 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 that the first three, something to be further investigated.
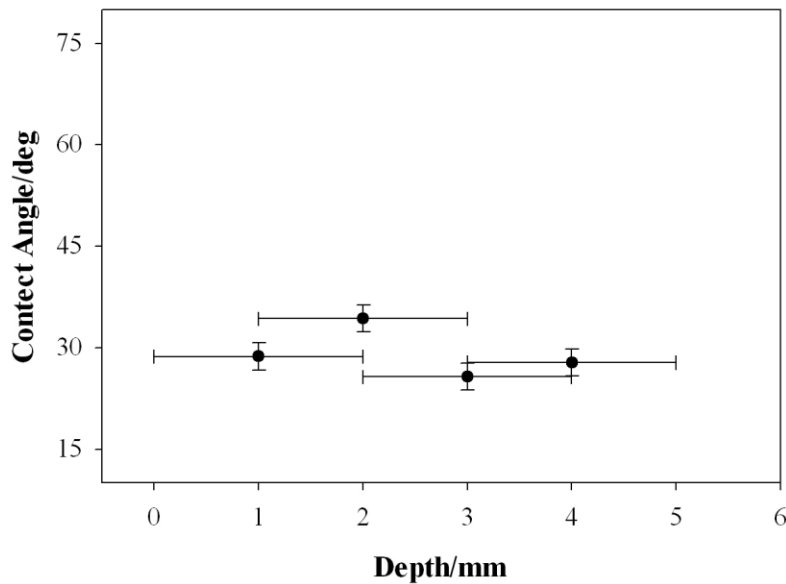

Figure 12: Contact angle measurement versus depth for I-40 sample.

For the I-40 sample (Figure 12) the contact angle is essentially unchanged with depth. Either there was no siloxane coating or it has completely deteriorated. These results need to be further compared with the XRF measurements and the other measurement performed on these samples. The average contact angles for the other sample, which showed little variation in angle with depth, are shown in Table 2.

Table 2: 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.

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 mm^2 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 13). For the sample in which a siloxane 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 obtained clear results.
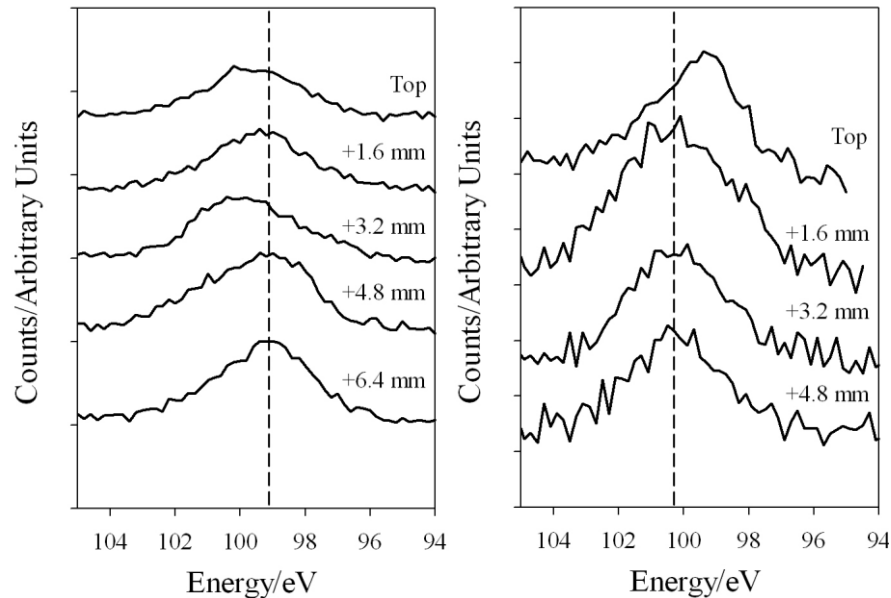
Figure 13: Left is the Si 2p XPS spectrum for the I-40 sample while the right is the Si 2p XPS spectrum for the SH-99-2A sample. All spectra were reference to the carbon 1s binding energy. These are the same samples that the contact angle measurements were performed on (Figures 12 and 11).

Staining of Silane Coatings

Numerous potential dyes for selectively staining silanes without staining the concrete were screened as a means of producing a positive stain for visualizing the silane layer. The test samples were prepared by painting the silane on glass slides and then curing at 80˚C until the coatings were no longer tacky. The staining tests were performed by immersing the silane-coated slides into dilute (0.1-0.4%) aqueous solutions of the dyes. Pieces of concrete were also immersed in these solutions to determine whether or not the dyes also stained cement paste. In this manner, dyes that selectively dye either the silane (a positive dye) or the cement paste (a negative dye) could be identified. Dyes that stained both materials can be rejected for use in mapping the distribution of silane in concrete. Table 3 shows the results obtained for several dyes.

Table 3: Results of Tests with Several Candidate Dyes

Dye	Silane Dying	Cement Paste Dying
Eriochrome Black	No	Yes
Eriochrome Blue-Black	No	Yes
Methyl Violet	Yes	No
Solochrome Violet	No	Yes
Brilliant Blue	Yes	Yes
Methyl Orange	No	Yes
Orange II	No	Yes
Alizarin Red	No	Yes
Neutral Red	Yes	No

Many dyes that we tested stained both the silane and concrete paste in the same manner that brilliant blue does and are not included in Table 3. It was found that eriochrome black, eriochrome blue black, methyl orange, solochrome violet, orange II, and alizarin red worked as negative dyes that adhered to cement paste but were prevented from binding to the paste where a silane coating still remained. Notably, neutral red and methyl were was found to stain only the silanes. Figure 14 shows a cross-section of a silane-treated concrete piece that was stained with neutral red to visibly indicate the depth of silane penetration while Figure 15 shows a close up. The stained top surface of the concrete piece is shown in Figure 16.

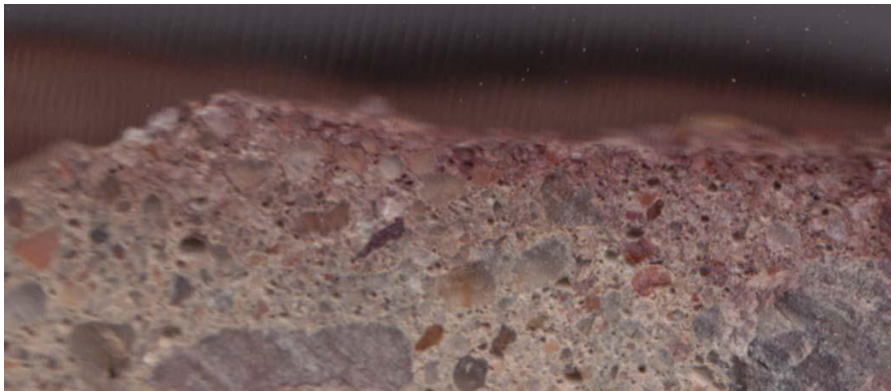Figure 14: Stained Concrete Cross-Section

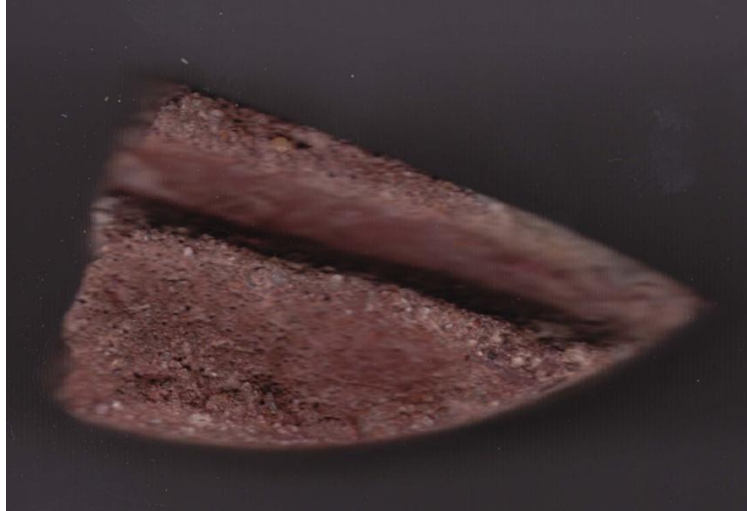Figure 15: Close-Up of Stained Concrete Cross-Section

Figure 16: Stained Concrete Top surface

Neutral Red (or toluylene red, Basic Red 5, or C.I. 50040) is a eurhodin dye that is used for staining in histology. It is also used to stain living cells and cell cultures for plate titration of viruses and is added to some growth media for bacteria and cell cultures.

We developed a colorimetic method that in which a change in color from orange to red indicated the presence of the silane. Above a pH of 8.0, neutral red exists primarily in its deprotonated form that is yellow. We therefore dissolved the dye in a sodium bicarbonate buffer (pH=8.1) to give an orange solution. When a drop of this was added to silane coated concrete, a red stain could be clearly seen depositing on the surface. No color change could be seen on concrete without silane present. The success of this approach may be due to a preference of neutral red to adopt its protonated form in hydrophobic media, a phenomenon previously observed in neutral red/surfactant mixtures.

Fluorescent dyes are also being assessed for staining due to the inherent higher sensitivity of fluorescent detection. Since some of the aggregate fluoresces under ultraviolet light, this task is complicated by the need for a fluorescent color that differs from that of the aggregates, some of which fluoresce. The dye 5-(N-octadecanoyl) aminofluorescein was able to make the silane coating fluorescent. Initially, the concrete was not fluorescent but after an hour the dye on the cement paste also became fluorescent. This may be due to reaction with the alkali in the cement. It may still be possible to differentiate the silane by confocal microscopy. We are currently planning to use very thin cement paste sections to achieve this goal.

The reaction of the silane with bromine was investigated for two reasons. The first was a desire to place a fluorescent tag on the silane by a two-step process whereby a brominated intermediate

reacted with aminofluorescein to give the desired product. The second was to explore the possibility of using the brominated silane for high-contrast mapping of the silane distribution by XRF microscopy. Commercial silane was applied to a cleaned glass square and cured in an oven at 65 °C. Once dried, the coated glass slide was run on an XRF spectrometer to check for bromine and none was detected. The slide was then placed in a glass chamber with 0.5 mL of bromine. The slide was on a raised platform in the chamber that prevented the liquid bromine from coming into contact with the slide. The chamber was closed and irradiated with an ultraviolet lamp for 24 hours. The slide was then removed and allowed to sit until excess bromine was gone. The slide analyzed by XRF spectroscopy and a large signal for bromine was detected. Reaction of a brominated silane film with aminofluorescein did result in the formation of a fluorescent film but when the procedure was repeated with a silane-treated piece of concrete the aminofluorescein stuck to both the silane and the cement paste. Further experimentation showed that the fluorescent dye binds strongly to untreated cement paste. Therefore, it is necessary to find another fluorescent dye to pursue this approach. Nevertheless, the silane-treated paste that was brominated may provide an improved approach to mapping the silane distribution by XRF microscopy.

In order to understand the bromination reaction of the silane, control experiments were performed with polydimethylsiloxane and hexamethylcyclotrisiloxane. It was found that these materials actually cross-link or polymerize under the reaction conditions. This is an exciting result since it suggests a new VOC-free method of applying a siloxane coating to concrete. The process could start with a photochemical radical initiator dissolved in a liquid linear polydimethyl siloxane polymer or in octamethylcyclotetrasiloxane (also a liquid). Application to concrete and exposure to sunlight would convert the material to a cross-linked hydrophobic rubber. Such silane-coatings could possibly be self-healing – wear would allow more liquid to diffuse to the surface and polymerize. Importantly, this process would also incorporate any silane already present into the continuous polymer and may be a superior method for refreshing a silane coating on older silane-treated highway infrastructure.

**Summary of Laboratory Investigations**

A number of promising investigation techniques have been established for the laboratory investigation of silane coatings in concrete. Testing has begun on the field samples obtained by ODOT from bridges with silane coatings of different ages. Soon this evaluation will be completed for these samples and the results compared. These tests have lead to a much better understanding of silane samples and allowed the research team to come up with several preliminary ideas for simple field investigation techniques.

Task III - Investigate Non-Destructive Field Techniques to Evaluate Silane Performance

For this task the research team has focused on evaluating two different test methods to be used in the field to determine the effectiveness of silane coatings on field concrete. These two methods consisted of the water permeability tests, and a 4 point resistivity test. Neither of these tests are standards. Although there are efforts underway to make the 4 point test an AASHTO standard.

From the testing it was found that the water permeability test was not accurate and was highly variable. Efforts were made to contact the distributor about the product and very little improvement was made. The research team ultimately feels that the primary problem is with a supposed water tight gasket between the surface of the concrete and the pressurized water chamber. If this gasket leaks, it is impossible for the person that is running the test to know. Even small leaks make significant impacts on the results.

The resistivity testing shows a much greater promise. This test was able to consistently tell the difference between concretes of different permeability. This was observed by comparing saturated cylinders of concrete mixtures of different water to cement ratios as shown in figure 17.
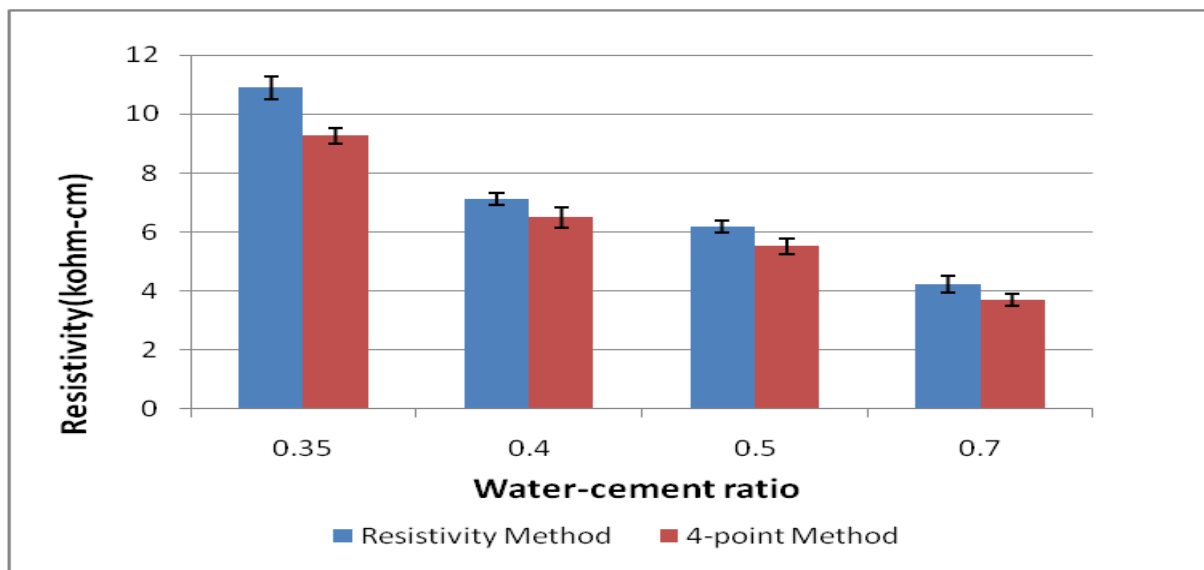

Figure17: Comparison between resistivity method and Wenner probe method

One thing that was found with the test is that the results are very sensitive to moisture. To investigate this further, additional tests were done on concrete cylinders of different water to cement ratios that were first dried in an oven to a constant temperature and then placed in water. Over time the weight and resistivity change was measured. These results show that the test is very sensitive to the moisture content in the concrete and that it takes concrete about 30 minutes to gain enough water that allows it to have a resistance measurement that is significantly different than the dry cylinder. This data is shown in Figure 18 and 19 for cylinders with different water to cement ratios and coatings with and without silane. The measurements for both dry cylinders and cylinders that have adequate silane coatings showed very high resistance.

20

The specimens that were subjected to moisture and did not have a silane coating did show a significant reduction in the resistivity over time. This ability for the 4 point method to capture this impact of water absorption shows that it is a very useful tool.
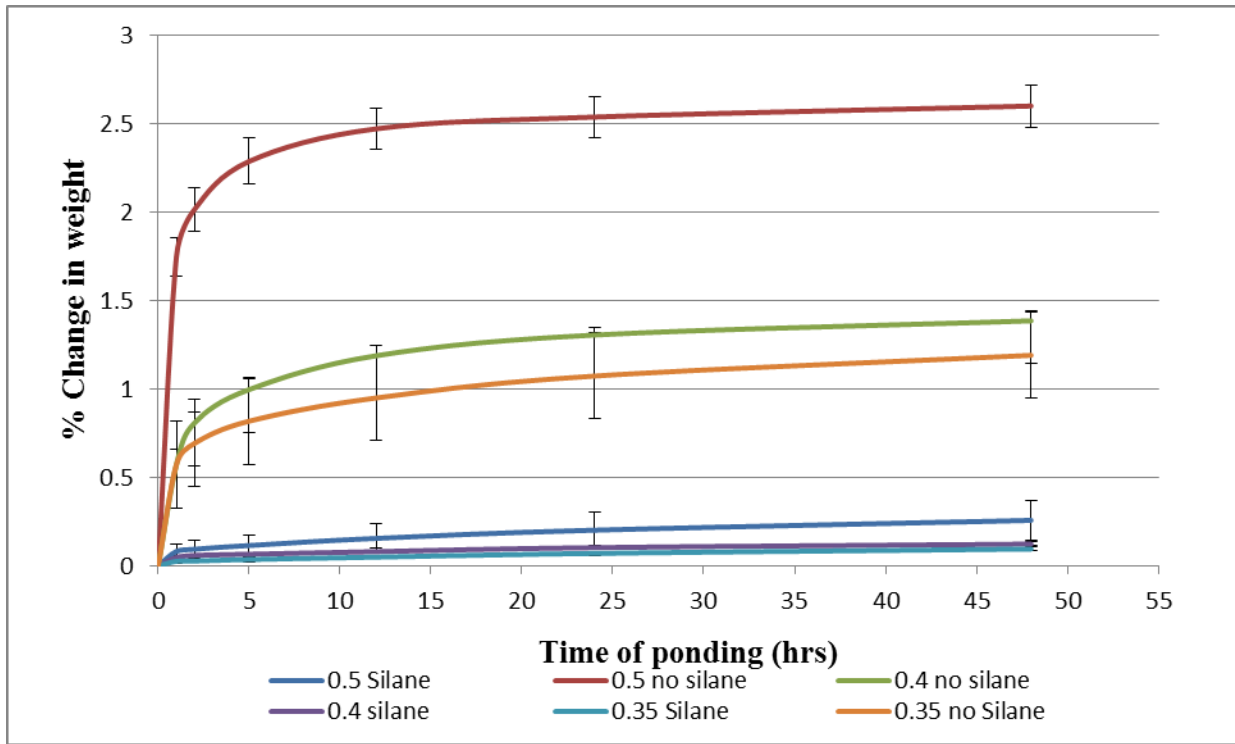
Figure 18: Time of ponding vs. Change of weight
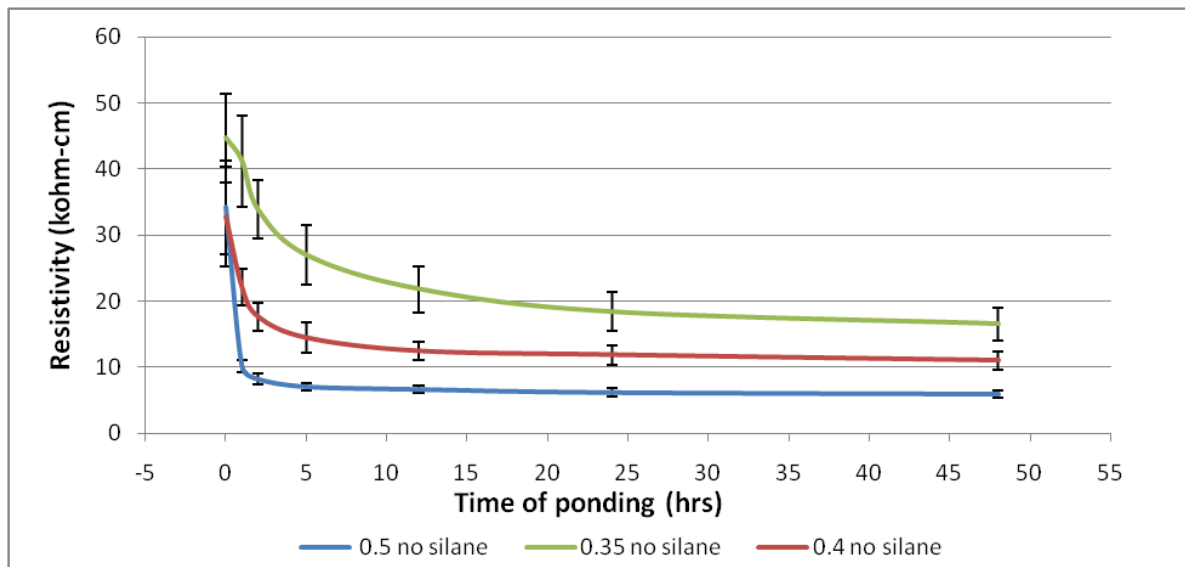
Figure19: Time of Ponding vs. Resistivity of concrete

This could allow a test to be run where a concrete bridge deck is first evaluated with the 4 point resistivity method and then ponded with water in a localized area. If there is active silane on the surface then this water will not penetrate and the resistance measurement will stay high or not change. If the silane is not present then the water will enter the concrete and will change the resistance of the surface concrete. This will be easily measured with the resistance probe.

Future Work

Significant progress has been made on Tasks I-IV during this fiscal year. In the next year efforts will be made on investigating the effectiveness of silane coatings in actual bridge decks. This work has somewhat started as mXRF and contact angle measurements have been made on a number of samples. This data will be compiled and culminated into a master report. The research team is also anticipating on visiting a number of bridge decks in the state and using some simple techniques to use the resistivity meter to evaluate if there is effective silane present. Also a simple technique that allows very small diameter cores to be extracted and then the presence of silane investigated with the dying techniques discussed in this report. This will allow a very thorough and useful evaluation to be made about the presence and effectiveness of silane coatings on bridge decks in Oklahoma.

Also in the coming year work will be done to determine how easy it is to re-apply silane to the surface of concrete that has already been treated. This will be an exciting test as it will provide direct guidance on what should be done to establish the effectiveness of silane that has been in service in the field.