

Dow Performance Silicones

Concrete Protection with Silanes



By Tony McAuliffe, BSc Asian Technical Services Manager,
Building Materials Protection Market; Dow

Dow Silicone Solutions

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Abstract

Specialty silanes such as isobutyltriethoxy silane are proposed as a cost-effective means of protecting concrete against the damaging effects of chloride ions in marine applications and from deicing salts. Selection processes, application procedures and performance evaluations are examined. Performance against alternative protective systems also is assessed.

Introduction

Specialty high-quality silane chemicals have been used for concrete protection for more than 20 years. Originally, they were proposed as a method to protect concrete structures against the ingress of chloride ions resulting from deicing salts. Used during the winter months throughout the northern hemisphere on highways, bridges and bridge approaches, deicing salts prevent vehicles from slipping in icy conditions. Today, silanes are also extensively used to prevent the passage of chloride ions into concrete on structures near or adjacent to the sea that are subject to splash and airborne chloride ion contamination.

The first question any designer or bridge or wharf owner in a marine environment will invariably ask is why a secondary protection system is needed for the concrete in their structure. In this context, the term "secondary protection" is used because it is well understood that the primary protection for reinforced steel concrete structures comes from the principle that steel will not rust in a passive, highly alkaline environment. Also, if the design is within established guidelines for marine concrete with regards to grade of steel, type of concrete and correct marine standard concrete rebar cover, and the structure is built according to these principles, then rusting of the steel should not easily occur.



In principle, this is correct. However, most observations in the construction industry include the evolution of processes to stop the seemingly impossible from actually occurring. What does this mean? If we retrace our steps to the early 1980s, the same arguments that negate the need for some additional or secondary protection were being argued. The principles of good design, good construction techniques and the use of world class quality assurance (QA) processes would mean that correctly built structures should not have problems of concrete failure due to chloride attack on the reinforcing steel. Of course recent history shows that this is not the case and there are hundreds of thousands of square meters of failed concrete on hand.

Today's concrete is technically much better than it was 20 years ago. To some extent this is a valid argument and the now common use of high-percentage secondary cure, pozzonlanic-modified concretes would seem to support this position. So why then do we now see many engineers designing cathodic protection systems into such structures? Perhaps the simple answer is that the use of these modern concretes is yet to reach the level of security that engineers see as acceptable risk. Some engineers are even designing cathodic protection systems into new structures that may never be used, or if they are used 20, 30 or 40 years henceforth, no one knows whether the system could be made operational at that time.

Many methods have been tried to give secondary protection to steel reinforcement. These include applying coatings to steel, using stainless steel instead of carbon steel, applying high build coatings to concrete, using cathodic protection systems and numerous others. The system with the best proven track record in preventing chloride ion intrusion (and hence prolonging the life of the steel-reinforced concrete) is the use of silane impregnants, such as the C₄-alkyl-modified alkoxy silanes.

Silanes are a relatively inexpensive insurance policy.

For designers and owners, they provide a means to reduce risk. While designers will tell you that a bridge designed and built to exact marine concrete specifications will not require protection, history shows that even the best-laid plans are subject to the vagaries of poor workmanship and material variability. If we accept the premise that at some point in the life of the structure problems of steel reinforcement corrosion will occur, then a system that can and will delay this for an additional 25 to 30 years at relatively small cost (compared to some of the other systems discussed) is a wise investment by owner and designer alike.

It is a fact that at some point in the life of the structure the owner will probably pay for costly repairs. The responsibility of the designers and consultants is to either delay this as long as possible or ensure it does not occur within the given projected life of the structure. When the decision has been made that silane penetrants are a sound engineering decision to prevent or delay the onset of rebar corrosion, the next step is to decide which silanes should be used. Decisions such as chemical and physical makeup of the molecules need to be made. Product form and application specifications need to be addressed. Lastly, a good initial QA program and a test program to ensure long-term performance of the silane impregnating system are required.

Reasons for Applying Penetrating Silane Sealers

There are readily proven economic and technical reasons for applying silane penetrants to concrete where chloride ions are present. It is a proven fact that chloride ion penetration is the primary cause of premature failure of these structures. The chloride ions can be present in the concrete either because

deicing salts are used on the structure or because of the natural ingress of salts due to splash and spray from the marine environment. Regardless of the reason, the end result will be the same Chloride ions will slowly permeate the concrete leading to rusting of the rebar. The main difference between the two scenarios is that the deicing salts are likely to cause a more rapid problem than the natural splash and spray effects experienced in a marine structure. Repairs are costly and most systems – whether they are applied as a preventive or repair measure – have a limited life. Silane treatments are an economical way to provide long-term protection against the ingress of chloride ions.

The key reasons for choosing silanes are that they have a proven track record backed by numerous laboratory and field studies. They are not only the most effective system known to prevent chloride ion intrusion, but they are also the most cost effective. In summary:

1) Repairs are costly and interfere with the normal operation of the facility. Concrete repair and rehabilitation projects cost tens of billions of dollars a year globally. While there are many factors contributing to premature concrete failure, it is universally acknowledged that chloride ion penetration is the key component in reduction of service life of reinforced concrete structures in marine environments (or where high levels of deicing salts are used). Typically, even minor repairs will cost owners more than US\$100/m².

The cost impact of interfering with the operation of a structure can vary from simply being inconvenient, to – in the worse-case situation – making the structure unusable for long periods while the repairs are carried out.

2) Other systems exhibit limited life. In a survey of a number of bridges in Sydney, Australia, where concrete repairs had been carried out in the early 1990s⁽¹⁾ the overall conclusion was that it was very difficult to achieve high-quality repairs, especially when access was difficult. In observations of repairs on these structures in and around the city of Sydney, there was a commonality of faults noted such as insufficient cutback of concrete behind the steel reinforcement, cracks in and around the repair areas, repairs providing insufficient cover of the existing steel, poor preparation of the concrete surfaces and steel prior to work commencing, and in some cases, total incompatibility of the repair patch with existing concrete (different permeation, different thermal properties, etc.). They also noted cracking and general concrete deterioration in and around the repair areas.

These observations are typical. Repairs are difficult and are often subject to budget constraints. Further, they are dependent on the skills and knowledge of the workmen. If repairs can be avoided by pre-treatment with silanes, then they represent an economical investment by the owner.

We can predict how long various preventive systems will last on non-trafficable surfaces. See Table I.

Table I: Lifespan of Preventive Systems on Non-trafficable Surfaces

Oil-based sealers	<5 years
Coatings a) good-quality high builds b) low-quality, minimum film build	10-12 years 5-10 years
Non-silane penetrants such as silicates	Not applicable for these applications
Silane/siloxane, low-solids systems	10-15 years
Silanes, high-concentration two coat systems	20-30 years

However, for high-traffic surfaces such as bridge decks, the expected life will be less because the concrete surface erodes at a much faster rate, which removes the silane protection. Some surveys from studies in the U.S. predict typical protection times of between eight and 12 years for deep-penetrating silanes on trafficable bridge decks.

In view of the high cost of repairs and the fact that repairs often do not work well, many owners of infrastructure projects elect to specify that the concrete is sealed with silanes at the earliest possible time. This often will be done while the structure is being erected. This is by far the most economical time to coat with silanes.

3) Water and waterborne chlorides are the key reason for failure in marinegrade concrete. It has yet to be proven that recent design modifications will in any way lead to reduction in chloride ion penetration into these new concrete types. Without doubt there is evidence that many of these high-pozzolanic-type concretes are subject to hairline surface cracking and crazing. These fine cracks are a potential source of chloride ion ingress. Because silanes can bridge cracks up to 0.5 mm, they will generally work well in sealing these surfaces. Only time will prove that these concrete blends will have any significant reduction in chloride ion penetration.

4) From a pure cost perspective, the best time to apply silanes is during the construction phase. This is when labor costs will be lowest. In many types of construction, the piles, beams and headstocks will be poured in a precast yard and then transported to the site. Silanes can be applied at this time under ideal conditions and with total access to all faces of the precast sections. On-site concrete treatment can be done much more easily because the scaffolding, cranes and/or boats will already be in place and the access costs are reduced. In most post treatment applications, labor becomes a significant component of the overall cost, especially if repairs are also required.

In summary, the ideal time to coat concrete with silanes is during the construction phase.

New or Old Structures?

While the best time to coat concrete with silanes is at the construction phase, coating is also a commonplace practice used to extend the life of older structures. The advantage of using silanes on new structures is that it allows maximum access to all parts of the structure. With no existing chloride problem, the maximum cure rate of silanes can be achieved on highly alkaline concrete. The application set-up, testing and QA protocols should be clearly understood by all parties involved. For new structures, the key initiator for using silanes is as a preventive measure. Typically, the minimum cure time before silanes are applied is 28 days. However, on some projects where rapid cure concrete is used, silane is successfully applied in as short a time as seven days after placement. In these cases, trials should be done beforehand to ensure adequate depth of penetration (DOP) and performance, such as water and chloride ion exclusion.

Silanes are used on older structures when either a corrosion problem already exists or more often when it is believed to be imminent, as in when tests indicate the chloride front has penetrated deeply into the concrete. Numerous studies on both new and old structures have shown silanes will effectively extend the life of structures⁽²⁾. These studies have been taken in the form of tests of existing structures and /or by model predictions⁽³⁾ for relatively new structures.

The decision to treat the older structures with silanes is usually based on one of the following criteria:

- 1) The owners will have numerous structures that they own and that they need to rehabilitate them on a routine basis. Typically this is seen with government agencies that own a number of wharfs of various ages. It's very easy to predict that problems of corrosion on one wharf will be rapidly followed by problems on other wharfs in their jurisdiction.
- 2) The structure is a prestige project where regular corrosion tests are taken. The presence of chlorides at a given depth in the concrete can easily be extrapolated to accurately predict when the chloride front will reach the steel reinforcement. The choice of applying silanes is similar to the methodology used for new structures in which the chloride front is halted to ensure corrosion will never occur.
- 3) The last scenario occurs when failures have already begun and the owners hope to increase the life of the structure by coating with silanes. Frequently, they have already spent considerable money on repairs and hope to keep additional costs at a minimum.

The basis for sealing the structure with silanes (even when extensive contamination with chlorides has occurred) is to halt or dramatically slow down the chloride front.

A good example of the process was the early 1990s test of a world famous structure in Sydney, Australia, the Sydney Opera House. The test showed significant chloride ion ingress into the concrete shells. To halt the progress of the chloride front, isobutyltriethoxy silane (IBTES) was applied to all exposed concrete in accordance with the consulting engineers' recommendations⁽⁴⁾ and from the local works department's specification⁽⁵⁾. In this report it was stated "the continuing use of silanes to provide longer service life for concrete in severe water and salt water environments is certainly recommended."

The Corrosion Process

To fully understand how silanes work in preventing rebar corrosion, we first need to have a basic understanding of the corrosion process and how chloride ions interrupt the concrete passivation process. Protection of steel reinforcement in concrete is very much dependent on the pH of the concrete. Freshly poured concrete has a pH in excess of 13 when saturated with water, due essentially to the high levels of calcium hydroxide salts that are present. Concrete is naturally porous. Air pockets are introduced during mixing and also when the concrete is poured. Capillary pores form as excess water bleeds from the concrete matrix, where the smallest pores, gel pores, are a result of the cement crystallization process.

Concrete aggregates can vary from fine sand to coarse basaltic, granite or limestone aggregates of various shapes and sizes. The final concrete is dependent on the types and grading of the aggregates, the water-to-cement ratio, the type and amount of cement and the various admixtures (additives) that are used. The physical and chemical nature of the concrete will vary throughout the structure. The ultimate strength and porosity is also dependent on blending and the method of placement and curing used. Lots of things can go wrong, even before we start looking at difficulties of pouring, ease of vibration, poor workmanship in setting up formwork and the steel reinforcement cage. Complicating all of this is the complexity of many of the segments, the amount and volume of steel in the sections and site conditions, which are at the vagaries of the weather. The idea that one can design a concrete that will negate all potential problems is a fallacy.

Effects of Chlorides Ions

Chloride ions interfere with the passivation process that a highly alkaline environment (pH >9.5) provides. As a general rule, steel will not rust if the pH exceeds 9.5. Fresh concrete with a pH in excess of 13 exists in a passive environment where rusting cannot occur. The alkaline environment of fresh concrete polarizes anodic areas in the steel reinforcement. Two key factors can change this environment. First, concrete can carbonate over long periods of time. The calcium hydroxide salts are converted to the non-alkaline calcium carbonate due

to the effects of CO₂ gas in the atmosphere. Second, chloride ions can have an adverse effect on the passivation process. The presence of chlorides can change the passivated film on the Fe into an iron chloride-hydrated complex, which leads to localized pitting corrosion at the anodes. Along steel bars there will always be areas that are more anodic than other areas. Passivation is difficult, nearly impossible, even with very low chloride concentrations. As a guideline:

If the chloride ion concentration, [Cl] is < 0.4%, there will be little risk of corrosion.

[Cl] is 0.4%- 1%, there is medium risk of corrosion.

[Cl] is >1%, there is a high risk of corrosion.

In most marine environments, chloride contamination is caused by airborne or splash contamination. Typical high strength, low-porosity concrete structures are used in these infrastructure projects. Chloride ions are many times more likely to be the initiator for corrosion than the long-term process of carbonation. Carbonation of low-porosity concrete proceeds at a very slow rate and may never be a factor in steel rusting on these structures.

When steel rusts (Fe → Fe III), the volume that the reinforcement bar occupies increases nearly threefold causing expansive forces on the concrete leading to cracking and spalling. In coastal areas, if the chlorides can be prevented from entering the concrete (even relatively carbonated concrete) then the rate of corrosion will be greatly reduced. Hence impregnants, which seal the concrete against water and waterborne chloride ingress, will reduce corrosion in both new and old structures.

Other mechanisms of deterioration of concrete include salt crystallization in pores, leaching of soluble salts by water, weathering effects, chemical attack and alkali aggregate reaction. Silanes can help reduce the effects caused by these external factors as well, although the key benefit in extending the life of marine structures is in preventing water penetrating into the concrete and therefore stopping water-borne chlorides being transported to the steel reinforcement.

Rust Prevention

For rusting to occur, three factors must all be present: an oxygen-rich environment, which fuels the process; water-saturated concrete, which carries ions between the corrosion cells, and an electric potential or battery along the rebars. Stop one of these and you can stop corrosion. The catalyst in the marine environment is the presence of chlorides that amplify the effect many fold. Typically, from a design and materials perspective, this is best controlled by use of low-porosity, dense concrete mixes and by increasing the concrete cover over

the steel. Steel will always have differing potentials at various points along the bars and preventing oxygen permeation is not easily achieved. So, most protecting systems rely on reducing water absorption into the concrete, because water is the means of transporting all ions (including chloride ions) throughout the concrete matrix. Many secondary protection systems have been tried with varying degrees of success. **The most widely accepted of these systems today is the silane impregnants.** Any concrete parts of the structure that are permanently immersed, such as piles and piers, will not generally be treated. The reason is that the level of oxygen dissolved in the water is not considered high enough to fuel the corrosion process. Some designers choose to coat all concrete including precast (permanently immersed) piles prior to installation. The tidal zone is the area of greatest contention, since the concrete in these areas will undergo a continuous wetting and semi-drying cycle throughout the life of the structure. The contention arises as to whether the concrete is ever sufficiently dry to allow sufficiently high concentrations of oxygen to be present. There are proven methods for treating these areas that differ from standard application techniques. Suppliers should be consulted as to the suitability of their product for these tidal zone areas and the best methods of application to ensure maximum penetration depth is achieved.

Principles for Using Silanes to Prevent Corrosion of Reinforcement Steel

If you prevent water from entering the concrete, the risk of corrosion is vastly reduced. If you prohibit the chlorides from entering the structure, the main accelerator for the corrosion process is removed. Alkyl alkoxy silanes do this very well.

Silicone resins, silicone polymers, siliconates and a raft of other silicon-based materials are universally recognized as providing the best penetrating-type water barriers on all types of porous building substrates. They find application in other industries as well – in personal care applications such as sunscreens to prevent wash-off, in textiles they are used to provide water repellency to fabrics exposed to the elements such as tarpaulins and umbrellas, and in the leather treatment industry they are used by the military around the world to protect boots against water ingress. The leather industry is a major user of water repellent treatments. The question is why penetrating silanes are preferable to coatings and why only a small number and types of silanes, compared to the huge number of silicone and silane products available in the marketplace, are suitable for protection of high-strength concrete will be examined further.

Silanes vs. Conventional High-Build Coatings

The simplest way to understand the difference between coatings and silane penetrants is to consider that coatings

Table II: Silanes vs. Coatings

Silanes	Coatings
Penetrate deep into the concrete matrix (4-5 mm into high-strength concrete)	Act on the surface of the concrete
Simple surface preparation (brush loose material from surface)	Complex surface preparation involving sand blasting or high-pressure water
Resistant to oxidation, UV, weathering	Breakdown due to effects of oxygen and UV
Long-term protection depends on DOP	Surface damage means loss of protection
Easy to apply	Complex application with skilled applicators
Long-lasting protection (>20 years)	Maximum 10 years life
No change in surface appearance	Surface is appearance/color of the paint
Growth technology	Declining technology

Table III: Typical Alberta Test Data for Silanes and Other Common Waterproofing Products

Generic Description of Sealer Type	Initial	After 1 st Abrasion	After 2 nd Abrasion
Acrylic Coating	84%	10%	0%
Epoxy Coating	90%	20%	0%
10% Siloxane in Spirits	90%	80%	30%
20% Silane in Alcohol	85%	80%	40%
40% Silane in Alcohol	87%	88%	65%
100% Pure Silane	90%	92%	92%

Evaluation of Damproofing Performance and Effective Penetration Depth of Silane Sealers in Concrete, Paul D. Carter, ATU, American Concrete Institute, November 1993

work on the surface of the concrete whereas silanes provide protection from within the concrete matrix. See Table II for a summary of coatings compared with silanes.

Typical high-build paint coatings are seldom used on new structures and face increasing competition from silanes on older structures. Perhaps the only advantage that paints have for old structures is that the coating will hide underlying defects in the concrete for a short term.

To fully understand how silanes compare to coatings for the protection of concrete, one only needs to look at the Alberta test protocol⁽⁶⁾. This test method examines long-term performance of protective systems by artificially abrading the surfaces as would occur naturally over long periods in the field. The results in Table III were obtained in an American Concrete Institute study,⁽⁷⁾ which used the Alberta test protocol. The results are for resistance to water absorption over a 24-hour period. For example, a result of 100 percent means 100 percent water exclusion.

In effect, the study showed that protection of the concrete with typical paint coatings was 100 percent reliant on the integrity of the coating, whereas silane protection is almost totally dependent on the integrity of the concrete. This is the key difference between the two protection systems and the reason that silanes will theoretically last as long as the concrete. Therefore, a lifespan of more than 20 years is readily obtainable and is likely to be much longer for higher-strength concretes.

Silanes vs. Other Silicone Materials

Historically, many silicones have been successfully used to protect porous masonry building structures around the globe. In fact, their use goes back more than 30 years. However, as concrete technology evolved and higher and higher grades became commonplace, many of these silicone resins and polymeric systems were found to be unsuitable for concrete. Three key factors that made many of these silicone chemicals unsuitable were a) the size of the molecule, b) their resistance to alkaline environments and c) their surface tension.

a) Size:

Most of the polymeric-type systems used historically (and in many cases still in use today) are very large molecules, which work for most masonry types where the voids are large. They are also suitable for low-grade concrete that contains many more and larger pores than the higher-grade concretes in use on today's bridges and wharfs. Air pockets are not a problem in high-strength concrete, but capillary pores (1-20 microns in diameter) and gel pores (25-50 Å or 1/10,000 of a micron) are a problem for these large resin/polymeric systems. These molecules are too large to penetrate these tiny pores. On the other hand, silane molecules are very small (in the order of 10 Å), so they have no problem penetrating capillary pores and even gel pores.

b) Alkali Resistance:

For most building substrates, alkali resistance is not a problem. Even for concrete panels, concrete grade ensures rapid surface carbonation. Therefore, a silicone does not need to be resistant to alkaline environments. High-strength marine-grade concrete is highly alkaline and maintains the surface and near-surface alkalinity for many years because carbonation is very slow. Most of the silicone systems used for general building work do not have good alkali resistance and simply do not perform long-term on marine-grade concrete.

c) Low Surface Tension:

Silanes have some of the lowest surface tensions known to the chemical industry. They are lower than even the polymeric silicone systems. Low surface tension means easier surface wet-out and deeper substrate penetration even in very low-porosity substrates.

Silanes will therefore provide the best long-term protection as they penetrate the deepest of any known chemical. In addition to their acknowledged and proven water resistance, they are not harmed by the alkaline environment and provide the longest protection currently available. Silanes work by slowly curing deep within the concrete matrix, forming a silicone resin that lines the smallest pores in the concrete and chemically attaches to free silica in the concrete matrix.

Which Silanes Provide Protection?

In the chemical world, there are literally hundreds of commercial silanes. Each is chemically different and is designed for a multitude of applications ranging from curing agents, crosslinkers, adhesion promoters, chemical intermediates and hydrophobers. Of these hundreds of chemicals, only a small number are suitable for hydrophobing new low-porosity concrete. The silane must be an alkyl silane and the alkoxy functionality must be either ethoxy or methoxy.

a) Alkyl Chains

The minimum alkyl chain size that will provide sufficient alkali resistance is the C₄, isobutyl group. These large, bulky side chains are necessary to prevent alkali attack on the Si-O bonds that form when the silane crosslinks to a silicone resin deep in the concrete pores. There are many silanes (and silicates) that have only methyl side chains. These methyl groups will provide excellent water (and chloride ion) resistance for a short time. However, they do not protect the silicone backbone polymer against **long-term** deterioration under conditions of high pH. There is some evidence in the literature that suggests propyl side groups will afford some protection, but their use is usually limited to non-marine applications. Suppliers should be asked to supply alkali immersion test data to prove that the products proposed meet this extremely important requirement.

In practice, the most common side groups that are seen are isobutyl, octyl and isooctyl. Hexyl chains are sometimes used as well. It is generally agreed the isobutyl group is the ideal size for water repellency, alkali resistance and maximized DOP. The longer groups will give better surface-water beading and a higher contact angle. The DOP will be slightly less in very dense concrete. Globally, the three major types of isobutyl, isooctyl and n-octyl are interchangeably used, depending on local requirements. In the United States, the octyl systems are favored as they comply more easily with stringent VOC laws. In Europe and Asia, the isobutyl silanes are more commonly used.

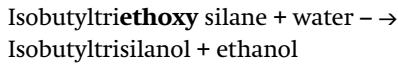
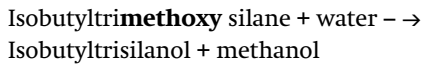
In the alkyl group, the isobutyl { (CH₃)₂CHCH₂- } side group in isobutyltriethoxy silane is responsible for providing the water repellency. The Si-O-Si polymeric backbone provides the orientation onto the surface, the chemical link to the concrete and the oxidation and UV resistance of the resin. Note that the

alkyl group must be C₄ (isobutyl) or longer to provide adequate alkali protection for the silicone polymer. In effect, this is a chemical with two completely different function results. The inorganic backbone orientates onto the surface of the pores while the alkyl groups are orientated toward the pore center and provide the water repellency.

b) Methoxy vs. Ethoxy Cure System

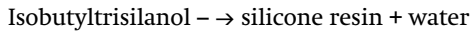
The first thing to understand is the role that alkoxy plays in the silane molecule to protect concrete. The answer is nil. The alkoxy portion of the molecule is solely a method of cure. Methoxy silanes release methanol as a byproduct of the cure mechanism whereas the ethoxy silane releases ethanol. The final active silicone resin that forms is identical regardless of the alkoxy group as shown in the following cure mechanisms that occur.

Step 1 is a hydrolysis reaction step that is catalyzed by the alkalinity of the concrete:



The reactive intermediate is the same for both chemicals.

Step 2 is a condensation reaction where water is eliminated. It is identical for both intermediates:



The cure system that is used almost universally today is the ethoxy system. This is because it is accepted in the industry that if a low toxicity chemical can be used, then it should be used. The ethanol byproduct of the ethoxy system is a very low-toxicity chemical whereas the methanol released in methoxy systems is recognized as being more toxic. The other reason is that the ethoxy system is slower to cure and will penetrate deeper into the substrate before it cures. Once cure is initiated and a resin begins to form, it will not penetrate any deeper. Most test data suggests a 10 to 20 percent higher DOP for ethoxy systems.

How Do They Work?

Unlike coatings, silanes protect within the concrete matrix. They penetrate up to 6 mm (slightly less in very dense concrete) and cure into a silicone resin that bonds to the sides of the pores. Unlike silicates, which not only show poor results in preventing chloride penetration and do not allow the concrete to breathe, silanes do not block the pores. Blocked pores can lead to surface deterioration of the concrete in marine environments.

The main entry point for water into high-strength concrete is through capillary suction. Wind and wave-driven rain and spray hit the concrete surface. As it drips or flows down the concrete face, capillary suction forces draw both the water and any dissolved salts into the matrix. Silanes prevent this water from entering pores by counteracting these capillary suction forces.

This is a vastly different mechanism to surface-acting paints, which form an impenetrable barrier on the surface. Unfortunately for paints, all protection is lost once the paint fails, whereas silanes will protect the concrete for as long as the 4 mm or more concrete face is still in place. This is a key reason why silanes are accepted as the longest-lasting protection systems currently available and why specifiers and owners can expect protection for more than 20 years when they use silanes of this type.

Factors Affecting Performance

See Tables IV, V and VI.

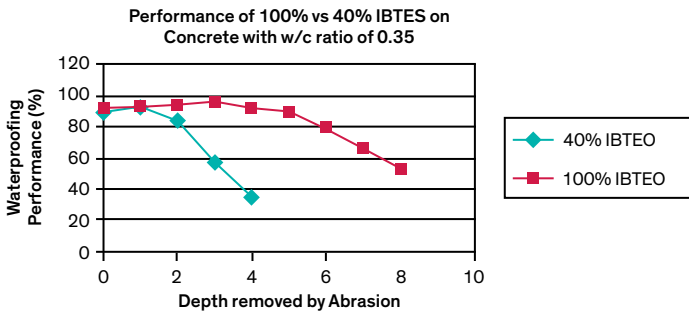
Table IV: Effects of Temperature and Relative Humidity on Depth of Silane (IBTES) Penetration (DOP)

Temperature	Relative Humidity	DOP
24°C	13%	6 mm
	52%	5 mm
	79%	5 mm
40°C	13%	5 mm
	52%	5 mm
	79%	8 mm

Table V: Effects of Surface Type, Coverage Rate and Dilution on DOP for Medium-Strength Concrete

% Dilution	Surface Type	2 coats @ 150 mls/m ² /coat	2 coats @ 250 mls/m ² /coat
Nil	formed-smooth	11 mm	11 mm
	surface-rough form	10 mm	11 mm
60%	smooth	8 mm	9 mm
	rough	8 mm	8 mm
80%	smooth	3.5 mm	5 mm
	rough	3.5 mm	5 mm
95%	smooth	3 mm	3.5 mm
	rough	3 mm	4 mm

Table VI: Concentration vs. DOP for Medium-Strength Concrete



1) Effect of Curing Conditions on DOP: In an environment where silanes are used, ambient conditions such as temperature, rain, wind and sea spray are all factors that must be considered. Test data generated in the mid-1990s⁽⁸⁾ show the effects of cure temperatures and relative humidity (RH). The concrete used was 50 Mpa and the IBTES was applied in two coats of 100 percent concentration.

2) Effects of Concrete Surface, Percentage Dilution and Application Rate on DOP: Tests carried out on low-grade concrete (25 Mpa) looked at a number of different factors to see what effect they had on the performance of IBTES. Two types of concrete were used. The first was concrete cast in a mold, which gave a very smooth finish, while the second was typically rough-form concrete (wood-trowel finish). The second factor was to look at what effect concentration had on DOP, and, lastly, the application rate of the silane that was evaluated.

While the type of concrete surface had little or no impact on DOP, the concentration and coverage rates had a significant effect on DOP.

When one looks at higher grades of concrete such as the 50 Mpa grades used on bridges and wharfs, then this factor becomes very significant. To achieve maximum DOP, high-concentration silanes (usually 100 percent) and low coverage rates (usually no more than 4 m²/liter) are used.

If we again look at the 1993 study by the American Concrete Institute⁽⁹⁾, the question of effective DOP vs. concentration of IBTES was examined. The study showed for the test grade of concrete, 35 Mpa, that a 100 percent silane achieved a significantly higher DOP than a 40 percent concentration silane. The reason that the higher-concentration silane penetrates deeper is that the silane itself is a far better surface wetter (see comments on surface tension) than a silane diluted in solvent. It will wet out and penetrate pores better. This is the same reason that a two-coat system always achieves better DOP than a one-coat system. The first coat saturates the pores nearest the surface whereas subsequent coats will then wet over

the existing treated surface and wet deeper. The greater the difference in surface energy of the substrate, the easier it will wet out. Therefore, the silanes penetrate deeper for each coat up to a maximum of two to three coats.

3) Liquid vs. Cream Silanes: While traditionally silanes have been supplied and sprayed as liquids, recent developments have allowed the silanes to be supplied in a cream form. The creams are usually high solid emulsions of the silane. The cream is far easier to apply in overhead applications and offers some benefits in waste reduction in vertical applications. There is some evidence in laboratory tests that the overall yields may be higher when used in exposed hot and especially windy conditions. Because all cream formulations contain a percentage of water, it is argued that the cream will tend to be less susceptible to evaporation than the liquid silane, increasing yield.

Creams offer some advantages in application. An added advantage is that they are visible on the surfaces much longer than the liquid silane so that it is much easier to see where the product has been applied. Most liquid silanes are absorbed well within 15 to 20 minutes, whereas creams may be visible on surfaces for a number of hours. This makes it far easier for applicators to see precisely where surfaces have been treated.

Typical Specification for Silanes

Laboratory and on-site experience has shown that as the grade of concrete increases, it can be more difficult to achieve deep silane penetration. As most specifiers look for a DOP in the region of 4 mm, it is desirable that for bridges and wharfs constructed with high-strength, low-porosity concretes, the silane is applied at very high concentration and application rates.

a) Application Rate Specification:

- Apply two coats of undiluted silane (100 percent actives) at 3-4 m²/liter/ coat.
- Allow 4 to 6 hours between coats. This allows the first coat to fully cure before the second is applied and contributes to higher DOP.
- Use low-pressure spray equipment to reduce material losses. Silanes are very low viscosity liquids.
- Apply using a continuous flood coating application method. The surface should look completely wet for some minutes.
- Protect the surface from heavy rain during the initial cure phase.
- Do not apply outside recommended temperature ranges. Ideal application temperature is 5 to 30°C.
- If exposed to high temperatures and/or very windy conditions, then apply under some form of shelter.

b) Material Specification:

- Product 100% Isobutyltriethoxy silane
- Purity >98%
- Siloxane Content <0.5%
- Hydrolysable Chloride <100 ppm
- SG 0.88
- Refractive Index (RI) 1.400

c) QA Procedures:

Before starting the project and throughout the course of the application, a number of cores should be removed from the structure and tested for DOP, water exclusion and chloride ion resistance as outlined in the following test methods.

Testing Performance

Three key test methods are universally used to test the performance of silanes on concrete. There are local variances to all these methods, but for the most part the same methods are used regardless of the country.

1) Depth of Penetration: The most common method of determining the DOP of silanes into concrete is to drill 50 mm cores from the coated and the non-coated areas of the concrete and then immerse the cores into water for one to two minutes. For most concretes, the DOP shows as a clear non-wetting band in the core, marking the maximum DOP. Most observers agree that this testing shows that the silane penetrates evenly into the concrete. Water absorption tests (either by immersion or by Rilem tubes) show this to be true for two-coat high-concentration applications. By removing slices at 2 mm layers and retesting water absorption of the top surface of the core, it is easy to show that the water absorption within the non-wetting band stays consistent and that there is a rapid drop-off once the fully wetted band is removed. The performance within this band of non-wetting will give full protection and there is a clear line of differentiation between the area where the silane will work and where it will not work. For example, the non-wetting band occurs to a 6 mm depth. For depths less than 6 mm, the concrete will be fully protected against water and waterborne chlorides. While at a depth of greater than 6 mm there will be no protection. There will be a clear DOP at which the owner can see that they have adequate protection. This is easily achieved by running trials before starting the project.

In some concrete types, this visual approach is not so simple. For instance, on many older concretes it is difficult to see the band of non-wetting as clearly as might be possible on a freshly poured light-colored concrete. This also seems to be a problem, particularly on concretes that use fly ash (or other pozzolanic) materials as a partial cement substitute. The color of the

concrete makes it very difficult to observe this non-wetting band. Sometimes using a water-based dye helps, but not always. Rilem tubes (See Figure 1) are a relatively simple method to check water absorption in any porous substrate. Alternatively, the ground cores can be tested using conventional water absorption immersion test methods. Historically, a number of pyrolysis test methods have been proposed for proving that the non-wetting band contained X percent of isobutyl, but none have been repeatable and the results are difficult to interpret. Rilem tubes give a reliable DOP figure and performance criteria.

Figure 1: Rilem Tube Test for Water Absorption



These tests show that generally speaking the DOP will increase significantly depending on the number of coats that are applied. In most commercial applications, two coats of liquid silane are recommended, whereas many cream silane manufacturers recommend one coat only. Trials should be conducted for any large project to ensure that adequate DOP is obtained. An alternative testing method should be considered as well.

2) Reduction in Water Uptake: Typically, water reduction uptake is measured by coating the vertical walls of the cored cylinders with an epoxy coating. The cores are then stood in a water bath with the face resting on a water-saturated mat and fully immersed at all times. Immersion time varies from laboratory to laboratory, but typically a 48-hour soak is used, although some tests may proceed for as long as 21 days. Typically, the immersion medium contains 15 percent NaCl solution to test the effects of the saline environment.

Results are expressed as relative weight change for the treated vs. non-treated cores. A satisfactory result will be a reduction of more than 90 percent in water uptake, although a figure of more than 95 percent is often seen when the silane is applied at maximum concentration and coverage rates. (See application procedures).

Note: If a quick onsite result is required, then data can also be obtained using Rilem tubes. Currently, there is no specification method applying to the use of Rilem tubes in this way; however, the ease of this test could offer an attractive method in the future.

3) Reduction in Chloride Ion Penetration: After completion of the water exclusion tests, powder samples are removed from the cores at various depths. In this way a profile of chloride ion concentration can be obtained from various depths within the core. Total chloride content of these samples is obtained using titration tests and a profile of chloride ion reduction within the various bands is obtained.

4) Other Test Methods: In addition to these three tests that can be done on most large projects, a number of other tests are sometimes carried out depending on information that the researcher wants to obtain. These include alkali-resistance tests, QUV accelerated-weathering tests and exposure tests in various chemical environments. Many publications cover these tests.

Conclusions

The concept of using silanes for protecting concrete against chloride ion ingress is not new. The chief areas of application involve the protection of bridge decks against deicing salts, where a life of more than 10 years is expected, and the protection of concrete marine structures against sea water salts, where life times of 20 to 30 years are expected.

While the technology has been used in excess of 20 years, the world of concrete is continually changing. The challenge to bridge and wharf owners and designers is to ensure that they are still adequately insured against the ever-present problems that chloride ions can cause. It is for this reason that silane protection still remains a key high-performance (and economical) protection system.

Silane types and delivery systems have changed to make them more applicable to today's environment. Similarly, there are new test methods that can be used to ensure that the silane treatments are providing the desired protection.

References

- ⁽¹⁾ Concrete Protection Seminar, UNSW, 1994.
- ⁽²⁾ Road Management Journal, US Roads, October 1 1997, "Sealers Shown to lengthen the Service Life of Concrete Bridges Exposed to Chloride."
- ⁽³⁾ Service Life Prediction Model for Reinforced Concrete Constructions, Treated with Water Repellent Compounds, 1996, L. Schueremans, D. VanGemert.
- ⁽⁴⁾ Engineering and Architectural Progress in the U.S. Related to Environmental Conditions (Second keynote paper presented at Concrete 99, Sydney 5-7, May 1999), by Donald W. Pfeifer, affiliated consultant, Wise, Janney, Elster Associates.
- ⁽⁵⁾ Tender Document for Sydney Opera House Upgrade Program, Shell Rib Protection, et. al., Contract #920187, March 1992. NSW Public Works Department, Operations Division.
- ⁽⁶⁾ Government of the Province of Alberta, Alberta Transportation and Utilities, Bridge Materials, August 1992, Specification for the Supply of Concrete Sealers.
- ⁽⁷⁾ Evaluation of Damp Proofing Performance and Effective Penetration Depth of Silane Sealers in Concrete, (American Concrete Institute, Fall convention, Minneapolis, Minnesota, November 1993), Paul D. Carter, Bridge Maintenance Engineer.
- ⁽⁸⁾ Taywood Engineering, Materials Technology Centre, Depth of Penetration tests for DCAPL, March 1994.
- ⁽⁹⁾ See reference 7.

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