Alkoxysilanes for treatment of reinforced concrete: 
*Beauty beyond Skin-Deep*

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Silane concrete/masonry sealers

Overview

• Why treat?
• What treatments materials are we talking about?
  • Silicone 101…
• How do they work?
• What are the options?
• What are and Where are the VOCs? what are the levels? How is it managed?
Why “Hydrophobe”? 

Damage to construction materials induced by water penetration 

- Corrosion of reinforcement steel bars in concrete 
- Freeze thaw damage (spalling, cracking) 
- Efflorescence 
- Micro-organisms growth 
- Loss of thermal efficiency 
- Dissolution (i.e. gypsum) 
- Dimensional instability (wood, FRC) 
- Chemical attacks (acid, sulfate attack)
Corrosion of Steel Reinforcement Bars

The two most important causes of corrosion of the reinforcing steel are carbonation and chloride contamination of the concrete. Chloride contamination occurs to structures exposed to de-icing salts or marine environments.

The corrosion products occupy a larger volume than the original metal. This generates stresses causing cracking and spalling of the concrete cover.
Carbonation of Concrete

Fresh concrete contains calcium hydroxyde, produced during cement hydration reaction.

When atmospheric carbon dioxide (CO₂) dissolves into the cement pore solution, carbonic acid (H₂CO₃) is formed. pH of pore solution decreases and some calcium hydroxyde is neutralized and is converted into calcium carbonate (CaCO₃).

When Ca(OH)₂ is depleted, a zone of low pH extends from the surface into concrete. This process is termed carbonation.

pH values below 10 at the steel (re-bar) may decrease steel passivation and resistance to corrosion.
Freeze (thaw, cycle) Damage

Formation of ice crystals can create pressure on the pore walls, generate stresses exceeding the mechanical properties of the matrix and induce irreversible damage.
Efflorescence

Efflorescence describes the crystallization of salts at the surface of a material, following the transfer of a solution at the surface of the material and the evaporation of the “solvent” (most often water) upon exposure to air.

Primary efflorescence is due to migration of calcium hydroxide produced during the cement hydration to the surface. Upon reaction with atmospheric carbon dioxide, it produces water insoluble calcium carbonate. It does occur during the initial phase of cement hydration.

Secondary efflorescence is due to transport of salts by the same mechanisms in already set/cured cement matrix.

- Much like Freeze damage – the growth of salt crystals at and near the surface can exert substantial pressure and cause spalling and cracking.
Water is **THE ENEMY** in this case...

- Chloride ingress is caused by salts dissolved in water. de-icing salts or seawater...
- Carbonation is enabled by CO$_2$ dissolved in water.
- Freeze/Thaw Damage occurs when water penetrates the substrate and freezes before it can dry out.
- Efflorescence is caused by water entering the substrate and concentrating/transporting salts to the surface as it leaves.

... so the best treatments will resist (liquid) water from entering the substrate... but will also prevent water from being trapped in the substrate ...
Silicon(e) 101 – What is it? What’s the difference?

**Silicon** -Si: An element. 2nd most abundant element on earth.

Silica – SiO₂ Naturally occurs as sand (quartz). Present in natural stone and concrete.

Silane – A functional monomeric Si-compound with 4 chemical attachments.

Siloxanes – Linear Si-O-Si polymer or pre-polymer. (i.e. silicone or PDMS)

Formulated silane/siloxane – A product formulated from one or more of the above, to meet a variety of applications.

Siliconate – A functional monomeric Si-compound reacted to a metal counter ion making it water-dispersible.

Silicate – A compound containing Silicon, Oxygen and one or more metals. Commonly used as densifying treatments for concrete, but *not* hydrophobic.

Organics – Compounds of C-C, (generally derived from petroleum) – acrylics, urethanes, epoxies, methacrylates, and paraffin waxes are most commonly used for protection and usually form visible coatings or films.
Silicon is basic - but versatile

Silicon → silane → silicone

Si chemistry is significantly different than Organic (Carbon)

- Silicon forms 4 bonds like Carbon, but no multiple bonds.
- Siloxane (Si-O-Si) bond strength is greater than C-C,
  - Requires more energy (>450kJ/mole) to break. → Very UV resistant.
- Si-O-Si bond is large – allows gas permeability.
  - Water vapor can pass thru – won’t trap water in substrates
- Si-O-H (silanol) bonds readily condense, C-O-H (alcohol) do not
  - $\text{Si-OH} + \text{OH-Si} \rightarrow \text{Si-O-Si} + \text{H}_2\text{O}$
  - Allows unique cure and reaction chemistry.
  - Enables a chemical bond to other silica containing substrates
What’s the difference...?

Silicon – Si: An element. 2\textsuperscript{nd} most abundant element on earth.
Silica – SiO\textsubscript{2} Naturally occurs as sand (quartz). Present in natural stone and concrete.

**Silane** – A functional *monomeric* Si-compound with 4 chemical attachments. *Alkoxy silanes usually have one organic and three alkoxy groups.*

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What Makes a Silane Unique?

- A silane can bridge the gap between inorganic and organic materials.
- They are widely used to add hydrophobic properties.
- They are very small molecules with extremely low surface tension – yielding a very high degree of penetration (4-8+ mm) when applied to porous substrates.
- **Alkoxy** silanes can serve as reactive treatments (*not* coatings). Appearance of the substrate is generally unchanged.
- Highly hydrophobic treatment – but water **vapor permeable**.

**Alkoxy (OR<sup>1</sup>)** – inorganic reactivity
- \( R^1 = \text{ethyl or methyl} \) (ethoxy or methoxy groups)

**Organic group** – hydrophobic or reactive
- \( R = \text{isobutyl or octyl typically} \)

Inorganic (reactive alkoxy)
- Concrete
- Stone
- Wood

**Organic (Hydrophobic)**
- Alkyl
- Phenyl
- Fluoro

**Alkoxy silane**
What’s the difference...?

→ Silicone = siloxane

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Siloxane… aka silicone...

Polydimethylsiloxanes (PDMS), Silicone, dimethicone, simethicone, dimethyl fluid...

Silanol terminated siloxanes are PDMS but terminated with OH groups in place of CH₃ (methyl) groups.

Resins are 3-dimensional molecules of various molecular weight, typically with some hydroxy (OH) functionality.

Skilful blending of Silanes, Siloxanes and Resins can result in very effective formulated multi-surface water repellents.

Siloxane chemistry and other Si-O bonded chemistry (like silanes) are gas permeable!
  - Keeps water out, but water vapor can escape.
What’s the difference...?

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Organics – Compounds of primarily carbon and hydrogen – with a carbon-carbon “backbone”, (generally derived from petroleum) – acrylics, urethanes, epoxies, methacrylates and paraffin waxes are most commonly used for protection and usually form visible coatings or films.
What is “hydrophobing”?

Maybe not be what you think…?  (not the same as waterproofing…)
-  Inorganic surfaces like concrete, stone, even glass tend to have a low inherent surface energy.
-  Water has a high surface energy.
-  High surface energy liquids like water tend to “wet” low surface energy materials
  -  water effectively wets concrete
-  When a liquid (water) wets a solid, it will cover as evenly as possible all available surface… and when a surface has pores or cracks – water will find them…

Author’s depiction of a wet concrete surface under high magnification
Mechanism of hydrophobing

Hydrophobing treatments work primarily by changing the surface energy – convert the low surface energy to high surface energy – if water doesn’t “wet” the surface, it doesn’t get “in” to the substrate:
How do Silanes work on concrete?

The chemical processes of hydrolysis and condensation:

1. Hydrolysis: a reaction with water that breaks (rearranges) bonds

Factors Affecting Hydrolysis:
- pH
- Temperature
- Availability of water

\[
\begin{align*}
\text{n-octyltriethoxysilane} & \quad \text{+ water} \\
\text{(aka nOTES)} & \quad \text{hydrolyzed silane} \\
& \quad \text{silanol functional}
\end{align*}
\]

\[
\text{Si} \quad \text{O} = \text{OH} = \text{silanol}
\]

\[
\text{Si-OEt} \quad + \quad 3 \text{H}_2\text{O} \quad + \quad 3 \text{EtOH}
\]

\[
\text{VOC} \quad + \quad 3 \text{EtOH}
\]

*OEt = OCH\text{2CH3} ("ethoxy")
2. Silane **Condensation** - with the substrate…and within the molecule (self-condensing)

Note:
Condensation reaction occurs at surface and within substrate as well, depicted only at surface for clarity.
Silanes as Water Repellents

The surface is converted from inorganic and hydrophilic to hydrophobic with an organic interface.

Water vapor can move through the treatment.

Concrete/Masonry/Stone Surface (inorganic)

Silane-treated block, split and dyed to show Depth of Penetration (about 8mm)

Actual image of water on silane-treated concrete surface
Performance of silanes

NCHRP Report 244 Series II:
Testing: Percent water absorption, and percent of chloride penetration, as compared to untreated control samples that have been submerged in NaCl solution and then allowed to air dry.
Typical values for silanes*: >85% reduction of chloride ion ingress as compared to untreated controls.

NCHRP Report 244 Series IV:
Testing: As for Series II, but after “Southern Exposure” weathering.
Typical results for silanes*: >90% reduction of chloride ion ingress as compared to untreated control.

Alberta BT001:
Testing: Percent water absorption, vapor transmission and chloride absorption as compared to an untreated control samples submerged in NaCl solution.
Typical values for silanes*: >80% reduction of chloride ion ingress as compared to untreated controls.

*based on online survey of various manufacturer’s claims, data sheets and some internal data
**Generic Description of Sealer type** | **Initial** | **After 1\(^{st}\) Abrasion** | **After 2\(^{nd}\) Abrasion**
--- | --- | --- | ---
Organic 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”
# Summary of Treatment Products

<table>
<thead>
<tr>
<th>Product Type</th>
<th>Uses</th>
<th>Advantages</th>
<th>Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Siliconates</td>
<td>Neutral substrates such as brick, clay tile, some concrete.</td>
<td>Water-based, low solids, efficient treatment of neutral substrates. No VOC</td>
<td>Alkaline (ph&gt;11), Lower performance and durability on concrete, low usage req'd or visible salt can be formed. Does not bead water; does not effectively exclude Cl</td>
</tr>
<tr>
<td>Siloxanes</td>
<td>Mostly used on vertical substrates for providing water beading - not usually used alone.</td>
<td>Some penetration, water beading, UV and oxidation resistance.</td>
<td>Not durable by themselves (does not react to substrate), can darken substrates if over-applied or high MW; very limited CI protection.</td>
</tr>
<tr>
<td>Silicates</td>
<td>Lithium and Sodium silicates are used to densify concrete by increasing silica content and filling pores.</td>
<td>Cheap, water soluble, work very well for intended application.</td>
<td>Not inherently hydrophobic -- does not exclude water or protect against CI beyond filling pores.</td>
</tr>
<tr>
<td>Formulated Silicone products</td>
<td>Multi-surface and general purpose, mostly on vertical applications to protect against efflorescence and freeze/thaw damage.</td>
<td>Best water beading overall, can be formulated to low VOC, versatility. Some chloride protection.</td>
<td>Penetration is limited especially with water-based. Chloride protection is dependent on silane concentration.</td>
</tr>
<tr>
<td>Organics - Acrylics, Urethanes, epoxy, methacrylate</td>
<td>General purpose water repellents, multi surface, enhancement coatings, paints, stains.</td>
<td>Low cost, can offer appearance enhancement, anti-graffiti and other coating properties. Can offer some CI protection.</td>
<td>Generally not penetrants, Do change appearance, and subject to wear. Can be slippery. UV degrades. Not reactive to substrate, not inherently vapor permeable</td>
</tr>
</tbody>
</table>
A word or two about VOC...

VOC = Volatile Organic Compound.

The term is sometimes used to refer to the VOC level as well –
As in: “the VOC is 400 grams/liter”

By definition: A VOC is any volatile compound of carbon that can participate in atmospheric photochemical reactions. (simplified)

- The chief undesirable outcome of these photochemical reactions is ozone... which is a major component of smog. This is the reason for regulation.
- The most common VOC’s are carrier solvents, and even without regulation, the public perception of solvents is not very positive.
- Some compounds have been determined to have negligible photochemical reactivity, and are considered as exempt – and they can be used as exempt solvents.
Usage basis of silane VOC…

If you just put a silane in a weighing dish, or run ASTM D2369 (EPA approved method to determine volatile content), mostly the silane will evaporate.

If you just go by theoretical, the “assumption” that every mole will react is inaccurate, (according to experimental results) – but “theoretical” VOC would be around 600 g/L.

→ ASTM D5095 uses a catalyzed solution and an “induction time” to mimic the reaction on a substrate (concrete) and gives a more accurate model of the volatile content. (D5095 is specified for silane/siloxane water repellents in method D2369)

✓ Using ASTM D5095, the volatile content of nOTES is roughly 38% - the VOC then comes out to 329 grams/liter:

<table>
<thead>
<tr>
<th>Product</th>
<th>nOTMS</th>
<th>nOTES</th>
<th>iBTMS</th>
<th>iBTES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>Clear</td>
<td>Clear</td>
<td>Clear</td>
<td>Clear</td>
</tr>
<tr>
<td>VOC* g/l</td>
<td>243</td>
<td>329</td>
<td>343</td>
<td>423</td>
</tr>
</tbody>
</table>

**Composition**
- n-octyltriethoxysilane (nOTES)
- n-octyltrimethoxysilane (nOTMS)
- isobutyltrimethoxysilane (iBTMS)
- isobutyltriethoxysilane (iBTES)

**Formulation**
- CH₃(CH₂)₇Si(OEt)₃
- CH₃(CH₂)₇Si(OMe)₃
- CH₃CH(CH₃)Si(OMe)₃
- CH₃CH(CH₃)Si(OEt)₃
Why CARB is relevant (relating to VOC)

CARB (California Air Resources Board) is the presiding EPA body of California.

CARB publishes “Suggested Control Measures” (with an opportunity for public comment) as *minimum* rules to be observed by individual Air Quality Management Districts.

Individual districts *can* enforce tighter rules. The South Coast AQMD (most stringent) is a good example.

The Ozone Transport Commission – (13 NE states) generally models CARB in setting new regulations.

Hong Kong adopted CARB regs (2009) as a means of establishing improved air quality.

On matters of air quality – California generally leads the regulatory trends!
**Reactive Penetrating Sealer** - as defined by CARB (2007 SCM)

http://www.arb.ca.gov/coatings/arch/Approved_2007_SCM.pdf

**Reactive Penetrating Sealer**: A clear or pigmented coating that is labeled and formulated for application to above-grade concrete and masonry substrates to provide protection from water and waterborne contaminants including, but not limited to, alkalis, acids, and salts.

Reactive Penetrating Sealers **must penetrate** into concrete and masonry substrates and **chemically react** to form covalent bonds with naturally occurring minerals in the substrate.

Reactive Penetrating Sealers line the pores of concrete and masonry substrates with a hydrophobic coating, but **do not form a surface film**.

Reactive Penetrating Sealers must meet all of the Following Criteria:

4.44.1 The Reactive Penetrating Sealer must improve water repellency at least 80 percent after application on a concrete or Masonry substrate. This performance must be verified on standardized test specimens, in accordance with one or more of the Following standards, incorporated by reference in subsection 8.5.20: ASTM C67-07, or ASTM C97-02, or ASTM C140-06; and

4.44.2 The Reactive Penetrating Sealer must not reduce the water Vapor transmission rate by more than 2 percent after application on a concrete or masonry substrate. This performance must be verified on standardized test specimens, in accordance with ASTM E96/E96M-05, incorporated by reference in subsection 8.5.21; and

4.44.3 Products labeled and formulated for vehicular traffic surface chloride screening applications must meet the performance criteria listed in the National Cooperative Highway Research Report 244 (1981), incorporated by reference in subsection 8.5.22.

Reactive Penetrating Sealers must be labeled in accordance with subsection 6.1.8

…and the answer is: alkoxy silane
CARB VOC limits snapshot

<table>
<thead>
<tr>
<th>Specialty Coatings</th>
<th>g/liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flat Coatings</td>
<td>50</td>
</tr>
<tr>
<td>Nonflat Coatings</td>
<td>100</td>
</tr>
<tr>
<td>Nonflat - High Gloss Coatings</td>
<td>150</td>
</tr>
<tr>
<td>Aluminum Roof Coatings</td>
<td>400</td>
</tr>
<tr>
<td>Basement Specialty Coatings</td>
<td>400</td>
</tr>
<tr>
<td>Bituminous Roof Coatings</td>
<td>50</td>
</tr>
<tr>
<td>Bituminous Roof Primers</td>
<td>350</td>
</tr>
<tr>
<td>Bond Breakers</td>
<td>350</td>
</tr>
<tr>
<td>Concrete Curing Compounds</td>
<td>350</td>
</tr>
<tr>
<td>Concrete/Masonry Sealers</td>
<td>100</td>
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<tr>
<td>Driveway Sealers</td>
<td>50</td>
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<tr>
<td>Dry Fog Coatings</td>
<td>150</td>
</tr>
<tr>
<td>Faux Finishing Coatings</td>
<td>350</td>
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<tr>
<td>Fire Resistive Coatings</td>
<td>350</td>
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<tr>
<td>Floor Coatings</td>
<td>100</td>
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<tr>
<td>Form-Release Compounds</td>
<td>250</td>
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<tr>
<td>Graphic Arts Coatings (Sign Paints)</td>
<td>500</td>
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<tr>
<td>High Temperature Coatings</td>
<td>420</td>
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<tr>
<td>Industrial Maintenance Coatings</td>
<td>250</td>
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<tr>
<td>Low Solids Coatings</td>
<td>120</td>
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<tr>
<td>Magnesite Cement Coatings</td>
<td>450</td>
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<tr>
<td>Mastic Texture Coatings</td>
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<tr>
<td>Metallic Pigmented Coatings</td>
<td>500</td>
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<tr>
<td>Multi-Color Coatings</td>
<td>250</td>
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<tr>
<td>Pre-Treatment Wash Primers</td>
<td>420</td>
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<tr>
<td>Primers Sealers and Undercoaters</td>
<td>100</td>
</tr>
<tr>
<td>Reactive Penetrating Sealers</td>
<td>350</td>
</tr>
<tr>
<td>Recycled Coatings</td>
<td>250</td>
</tr>
</tbody>
</table>

Note that the US EPA VOC limit for concrete protective coatings is 400 g/l
Summary

- Water is destructive to concrete structures – particularly steel-reinforced structures.
  - Water is the “way in” for all of the bad stuff…

- It’s not easy to make something durable enough to last in service on concrete.
  - Weathering and UV
  - Abrasion
  - Movement

- Due to their unique physical and chemical properties, alkoxy silanes can be used in situations where other treatments may not be durable or effective.

- Silanes have many advantages, and only a few limitations
  - Highly efficient – a little goes a long way… and they are easy to apply.
  - Durable against UV due to chemical properties
  - Durable against abrasion because they penetrate into the concrete
  - VOC (alcohol) is formed as part of the chemical reaction (cure)
  - You can’t “see” them, and they do not enhance appearance.

- Regulatory agencies, weighing the sustainability benefits against the relatively low VOC burden, have created categories and limits that allow the continued use of alkoxy silanes as protective treatments.