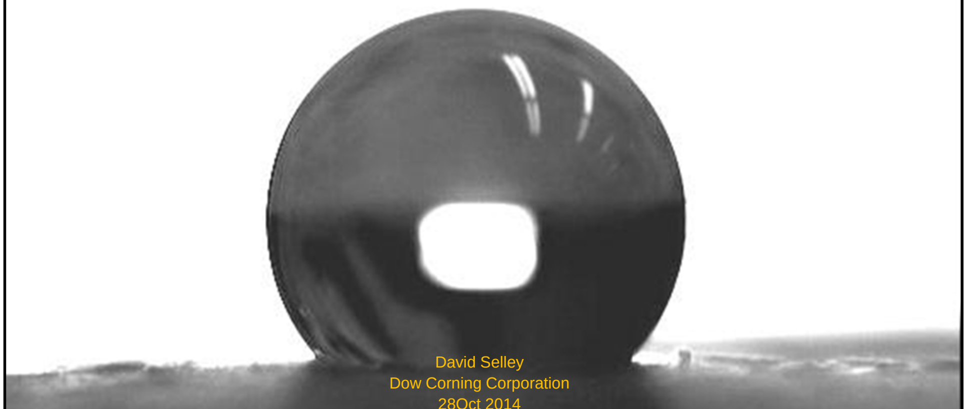
Silane and Siloxane:

Organosilicon treatments

for reinforced concrete



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Silane concrete/masonry sealers

Overview

- Why treat?
- Silicon(e) 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 “treat (“hydrophobe”)?

Damage to construction materials induced by water penetration

- ☞ Corrosion of reinforcement steel bars in concrete
- ☞ Freeze thaw damage (spalling, cracking)
- ☞ Efflorescence

- ☞ Micro-organism growth
- ☞ Loss of thermal efficiency
- ☞ Dissolution of binder
- ☞ Dimensional instability (composites)
- ☞ Chemical attacks (acid, sulfate attack)

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Corrosion of Steel Reinforcement

A primary cause of reinforced concrete failure is corrosion of the steel:

- The most prevalent cause of corrosion of the reinforcing steel is chloride contamination of the concrete.
- Chloride contamination occurs to structures exposed to de-icing salts or marine environments.
- The presence of chloride ion attacks the passivation layer that protects reinforcing steel.

- The corrosion products occupy a larger *volume* than the original steel.
  - There’s no place to go – so the stresses cause cracking and spalling of the concrete cover.
  - It gets worse as it gets worse…!

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Other damaging effects from water absorption…

Carbonation of Concrete

- CO_2 dissolves into the cement pore solution forming carbonic acid.
  The acid neutralizes free Calcium Hydroxide ➔ lowers pH of concrete.
- pH <10 at the steel (re-bar) decreases passivation and resistance to corrosion.

Freeze/Thaw cycling and damage

- Liquid water (snow/ice melt during the daytime) penetrates concrete
- When temp drops below freezing, formation of ice crystals creates immense pressure on the pore walls
- Induces irreversible damage ➔ spalling, cracking = damage to "cover".

Efflorescence

- Transport of salts and evaporation of water results in salt crystallization at surface.
- ➢ Much like Freeze/thaw damage – the growth of salt crystals can exert substantial pressure and cause spalling and cracking.

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Water is THE ENEMY …

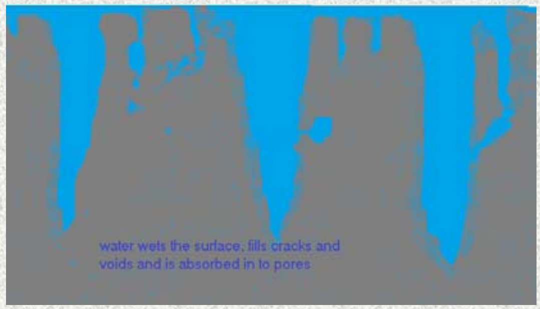
- ✓ Chloride ingress is caused by salts dissolved in water.
  de-icing salts or seawater…
- ✓ Carbonation is enabled by CO_2 dissolved in water.
- ✓ Freeze/Thaw Damage occurs when water penetrates the substrate and freezes before it can dry out.
- ✓ Efflorescence is caused by water entering the substrate and concentrating/transporting salts to the surface as it leaves.

… so the ideal treatments will resist (liquid) water from entering the substrate…
but will also prevent water from being trapped in the substrate …

What is “hydrophobing”?

Maybe not be what you think…? (not the same as waterproofing…)

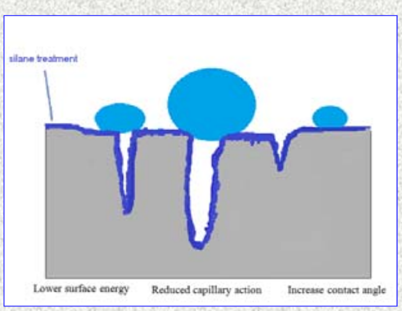
- Inorganic surfaces like concrete, stone, even glass tend to have a <u>low</u> inherent surface energy.
- Water has a <u>high</u> surface energy.
- High surface energy liquids like water tend to “wet” low surface energy materials
  - water effectively wets concrete
- When a liquid (water) *wets* a solid, 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

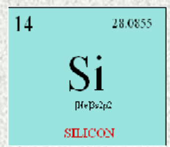
Mechanism of hydrophobing

Hydrophobing ***<u>treatments</u>*** 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:



Silicon is basic - but versatile

Silicon → **silane** → silicone
element — monomer — polymer

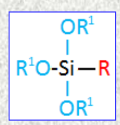


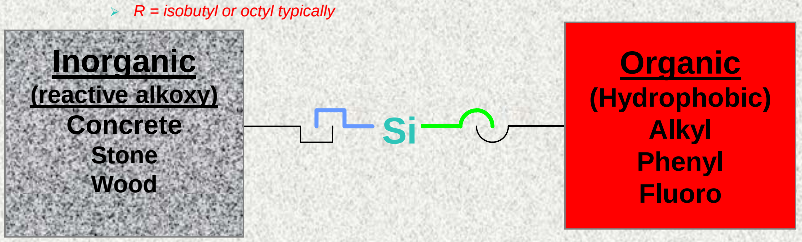
"Si" chemistry is significantly different than Organic (Carbon)

- ✓ Silicon forms 4 bonds like Carbon, but not double 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"
  - Si-OH + HO-Si → Si-O-Si + H_2O (water)
  - ✓ Allows unique cure and reaction chemistry.
  - ✓ Enables a **chemical bond** to silica containing substrates (concrete, glass, stone)

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^1) – inorganic reactivity
    - ➢ *R^1 = ethyl or methyl (ethoxy or methoxy groups)*
  - Organic group – hydrophobic or reactive
    - ➢ *R = isobutyl or octyl typically*



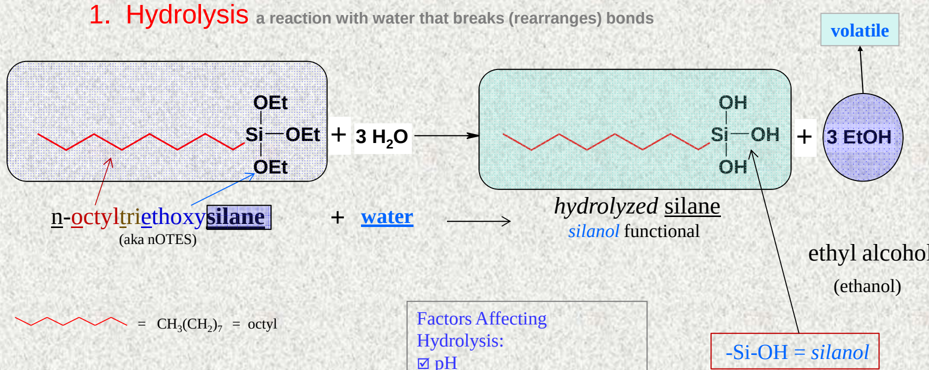


Alkoxy silane

How do Silanes work on concrete?

The chemical processes of hydrolysis and condensation:

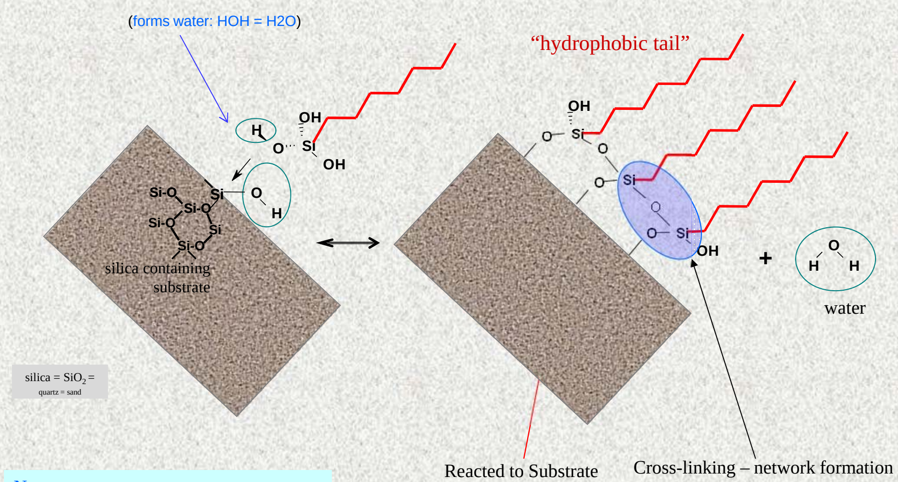
1. Hydrolysis a reaction with water that breaks (rearranges) bonds



OEt = -OCH2CH3 = ethoxy

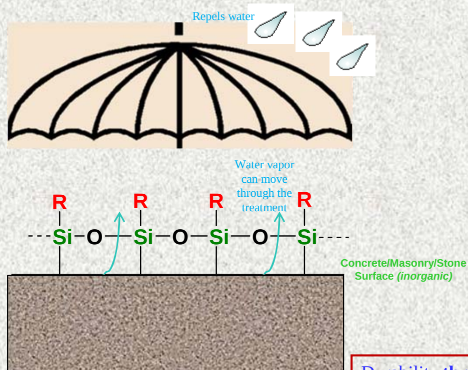
Factors Affecting Hydrolysis:
- ☑ pH
- ☑ Temperature
- ☑ Availability of water

2. Silane Condensation - with the substrate…and within the molecule (self-condensing)

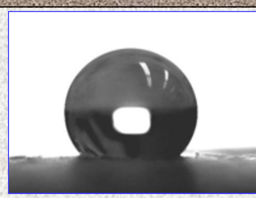


Note:
Condensation reaction occurs at surface and within substrate as well, depicted only at surface for clarity.

Silanes as Water Repellents



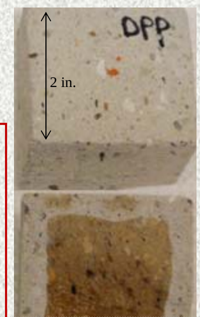
The ***surface*** *is converted from inorganic and hydrophilic (porous) to hydrophobic with an organic interface.*



Actual image of water on silane -treated concrete surface

Durability **three** ways:

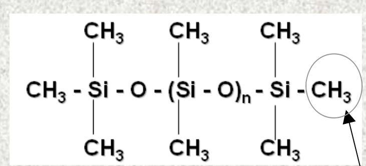
- ✓ Chemically bonded
  - ➢ it's "part" of the substrate
- ✓ Depth of Penetration
  - ➢ doesn't "wear" off
- ✓ UV resistant
  - ➢ very durable with weathering



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

Siloxane… aka silicone…

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



Silanol terminated siloxanes are PDMS but terminated with OH groups in place of CH_3 (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...?

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

Silica – SiO_2 Naturally occurs as sand (quartz). Present in natural stone and concrete.

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

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

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.

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

Organics – Compounds comprised of mostly carbon and hydrogen (many derived from petroleum) – acrylics, urethanes, epoxies, methacrylates and paraffin waxes are most commonly used for protection and usually form visible coatings or films.

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

Summary of Treatment Products

Product Type	Uses	Advantages	Limitations
Silanes	A "standard" for protection of reinforced concrete from chloride attack. Proven performance, specified by several DOT and highway departments.	**Depth of penetration, reacts** to substrate, **UV resistance**, very efficient, excellent Cl protection. Permeable, non-tacky, dry - low dirt pickup	Cure releases alcohol (VOC), "Neutral" substrates require catalyst for efficient cure.
Siliconates	Neutral substrates such as brick, clay tile, some concrete.	Water-based, low solids, efficient treatment of neutral substrates. No VOC	Alkaline (ph>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
Siloxanes	Mostly used on vertical substrates for providing water beading - not usually used alone.	Some penetration, water beading, UV and oxidation resistance.	Not durable by themselves (does not react to substrate), can darken substrates if over-applied or high MW; very limited Cl protection.
Silicates	Lithium and Sodium silicates are used to densify concrete by increasing silica content and filling pores.	Cheap, water soluble, work very well for intended application.	Not inherently hydrophobic -- does not exclude water or protect against Cl beyond filling pores.
Formulated Silicone products	Multi-surface and general purpose, mostly on vertical applications to protect against efflorescence and freeze/thaw damage.	Best water beading overall, can be formulated to low VOC, versatility. Some chloride protection.	Penetration is limited especially with water-based. Chloride protection is dependent on silane concentration.
Organics - Acrylics, Urethanes, epoxy, methacrylate	General purpose water repellents, multi surface, enhancement coatings, paints, stains.	Low cost, can offer appearance enhancement, anti-graffiti and other coating properties. Can offer some Cl protection.	Generally not penetrants, change appearance, and subject to wear. UV can degrade, not inherently permeable

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.

VOC of Common Silanes

Composition	***Formulation***
n-octyltriethoxysilane (nOTES)	$CH_3(CH_2)_7Si(OEt)_3$
n-octyltrimethoxysilane (nOTMS)	$CH_3(CH_2)_7Si(OMe)_3$
isobutyltrimethoxysilane (iBTMS)	$CH_3CH(CH_3)Si(OMe)_3$
isobutyltriethoxysilane (iBTES)	$CH_3CH(CH_3)Si(OEt)_3$

Product	nOTMS	nOTES	iBTMS	iBTES
Color	Clear	Clear	Clear	Clear
VOC* g/l	243	329	343	423

Influence of CARB?

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: alkoxysilane

South Coast Air Quality Management District (AQMD)

As California trends the country on regulatory… "South Coast" trends California

(SC)AQMD recently also added the Reactive Penetrating Sealers category to the most recent Rule 1113 regulations with a determination that certain structures can benefit from the protective aspects of these treatments… with a few extra requirements:

REACTIVE PENETRATING SEALERS are clear or pigmented coatings 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 meet the following criteria:

(A) Used only for reinforced concrete bridge structures for transportation projects within 5 miles of the coast or above 4,000 feet elevation; or for restoration and/or preservation projects on registered historical buildings that are under the purview of a restoration architect.

(B) Penetrate into concrete and masonry substrates and chemically react to form covalent bonds with naturally occurring minerals in the substrate.

(C) Line the pores of concrete and masonry substrates with a hydrophobic coating, but do not form a surface film.

(D) Improve water repellency at least 80 percent

→ The VOC limit for Reactive Penetrating Sealers per Rule 1113 (Sept. 2013) is 350 g/L
  → Source: https://www.aqmd.gov/rules/reg/reg11/r1113.pdf

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