

Keeping moisture at bay

Sustainable concrete protection with siloxane based admixtures

Contact:

Markus Roos
Evonik Industries AG
T +49 201 173-2360
markus.roos@evonik.com

Markus Roos
Sabine Giessler-Blank

Concrete structures and manufactured concrete products are frequently exposed to environmental attack. Water and salts cause the major part of all damages in construction work. This damage is estimated to be in a range of several billions of Euros per annum. Silicone-based water repellents can be used as an admixture to avoid application errors during post treatments of concrete.

Protection of a building against moisture is taken into consideration at the construction stage by the incorporation of hydrophobising agents into the concrete matrix (water repellents in concrete formulations). Today, metal salts of fatty acids are widely used as water repellents for in-situ concrete protection and represent the largest group of hydrophobising additives. Particularly if long term performance is required, this type of water repellent exhibits weaknesses such as air entrainment and inhomogeneous distribution in the concrete matrix.

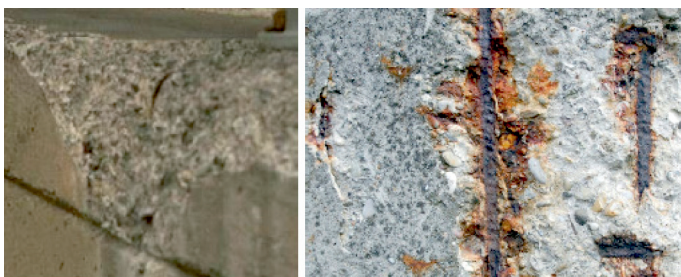


Figure 1: (left) Cracks caused by water in the substrate, (right) corrosion damage



Figure 2: Illustration of efflorescence damages

Waterbased additives which are composed of silane/siloxane are easily applied to the concrete matrix at low dosage rates at an early stage. By doing this, the water uptake is significantly decreased and compressive strength is not compromised. Tests have shown the superior hydrophobisation and efflorescence-control of this new class of products in comparison to, for example, metal salts of fatty acids. They can be used as a water-resisting concrete admixture according to EN 934-2. Due to their unique chemical design, the siloxane-based products provide outstanding water repellence and excellent beading, together with long term performance. Thus they offer sustainable protection to concrete structures and manufactured concrete products.

Moisture induced decay of concrete

Damage to concrete-based engineering constructions, residential and other buildings is very often related to water permeation and the transport of salts into and out of the concrete structure. This is a worldwide problem. Capillary action allows water to penetrate into the pore systems of the concrete matrix and causes severe damage. The reasons for the moisture-induced decay of concrete are not only chemical, physical and biological, but also improper construction work. Moisture dissolves the cement stone by the formation of bulky reaction products, which crack the concrete from inside. Subsequent

Results at a glance

- »» Organo-modified siloxanes in combination with alkoxy functional silanes are proven to give successful protection against water induced damages on concrete or mortars.
- »» The capillary transport of moisture and salts is reduced to a minimum.
- »» Low dosages, less influence on mechanical properties combined with the easy incorporation into the cement matrix make these products very suitable.
- »» The majority of damage caused by water can be reduced or totally avoided; thus the service life of concrete based materials can be extended.
- »» The fulfilment of the requirements for a water-resisting admixture underlines specifically the broad application range of siloxane/silane emulsions

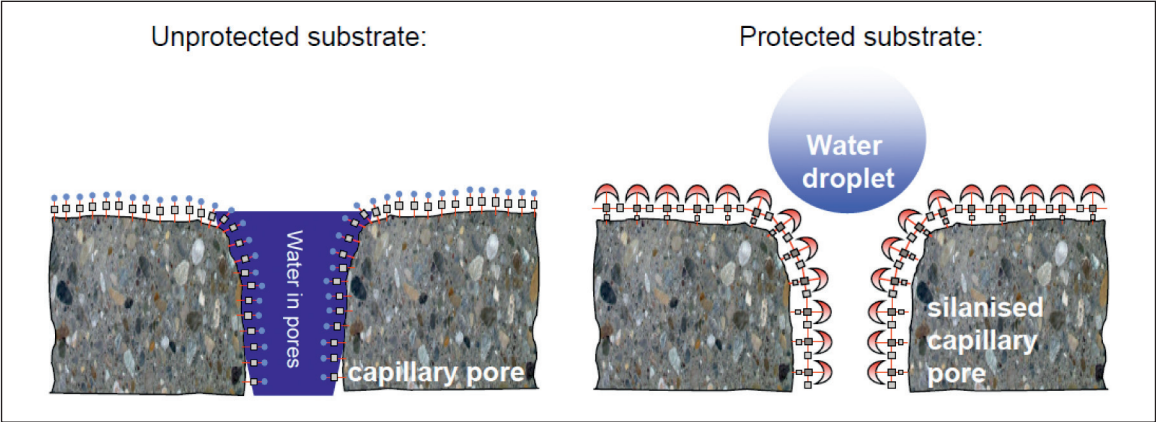


Figure 3: Illustration of water penetration in protected and unprotected substrates

damage occurs in the form of corrosion and internal chemical decomposition, efflorescence, alkali-silica reaction (ASR), growth of algae and fungus etc. The ice formed when water freezes in winter has a greater volume than water. This leads to cracks in the material. In nature, this freeze-thaw process turns hard rock into sand over the course of time. On the other hand, water introduces salts into the concrete and lowers its pH-value. In alkaline surroundings, iron is passified and does not rust, but if the pH-value

drifts down the metal starts to corrode. This is the well-known phenomenon of chloride corrosion.

How efflorescence occurs

Efflorescence is also a huge problem. It mainly occurs if water-soluble salts, moisture and capillary action are present in the pores. Salt blooming, i.e., secondary efflorescence is moisture-induced damage. Minerals and salts dissolved in water can be transported to the con-

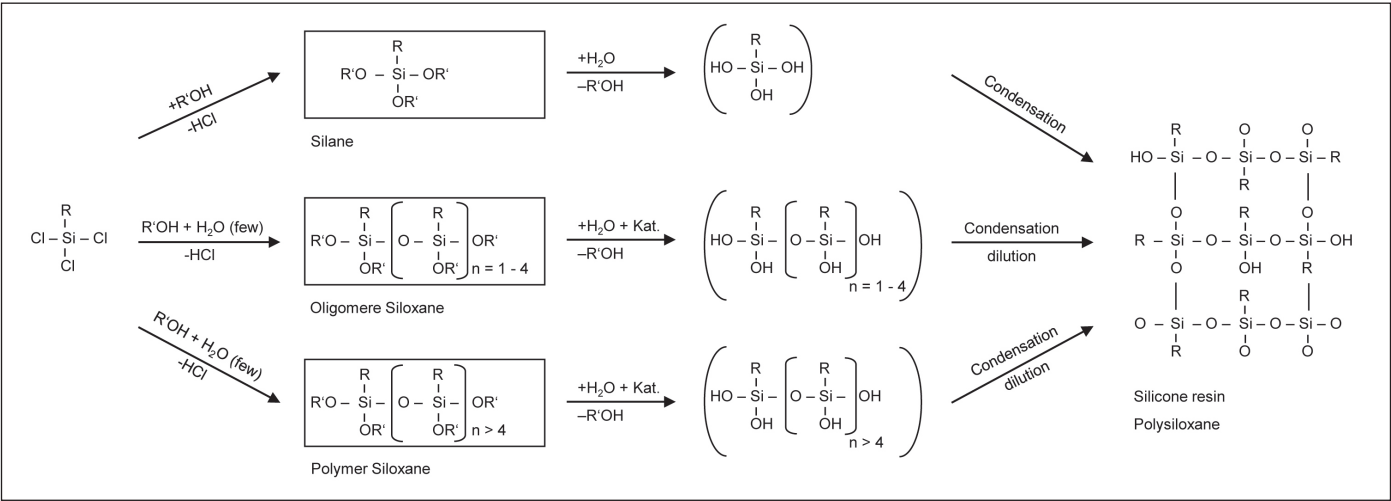


Figure 4: Production route of silanes and oligomeric/polymeric siloxanes

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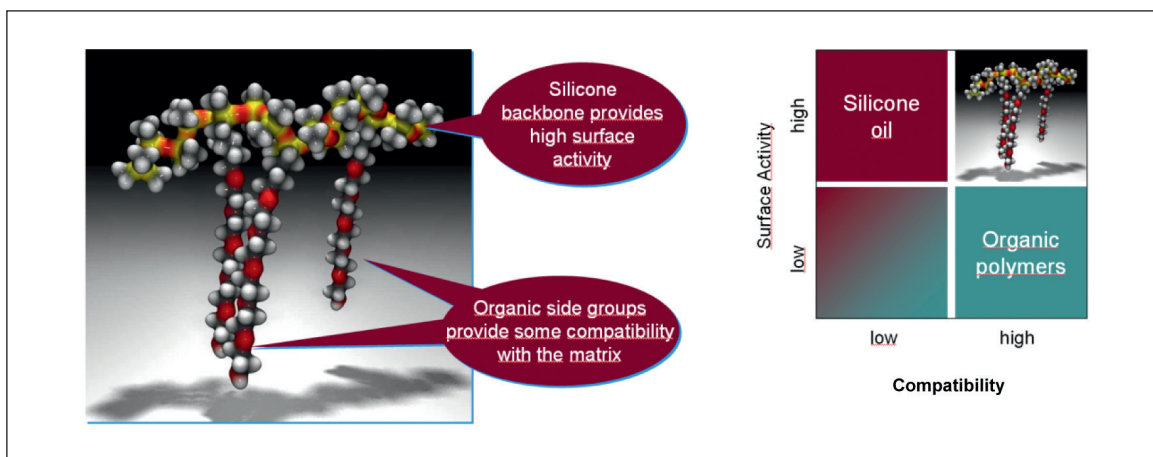


Figure 5: OMS combines good surface activity of silicones with the good compatibility of organic compounds

crete surface by capillary action. If the water evaporates, the salts re-crystallise and remain there. Crystallisation cycles, causing crystallisation pressure, will also induce damage to the surface and may also lead to structural cracks in the concrete.

Primary efflorescence (calcite salt blooming) can occur within the first 24 hours due to the calcium hydroxide which is dissolved in the pore water. Capillary action causes this pore water to move to the concrete surface and

react with CO_2 and water to form calcium carbonate, which crystallises on the surface and remains there as a white layer. This means that if water transport in the capillaries is stopped or hindered, most damage can be avoided.

It is well known that post application with silicone-based water repellents increases the resistance to water uptake, thereby reducing most damage. This treatment can extend the service life of concrete from approx. 10 to more than 100 years [1].

Penetration depth matters

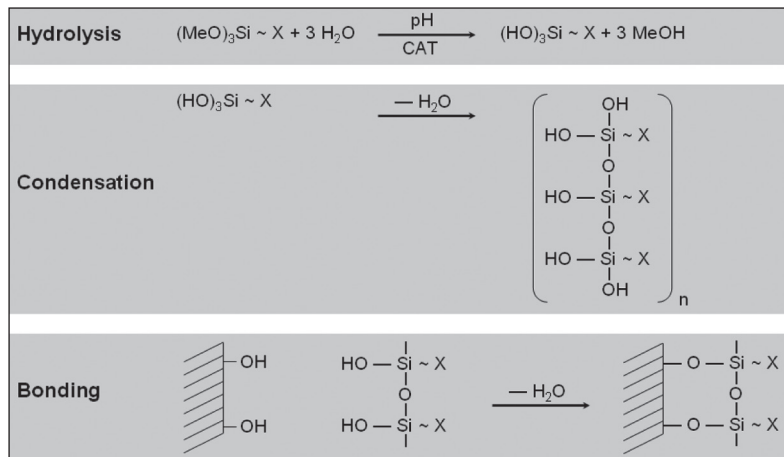


Figure 6: Mode of action of silane/siloxane compounds on substrates

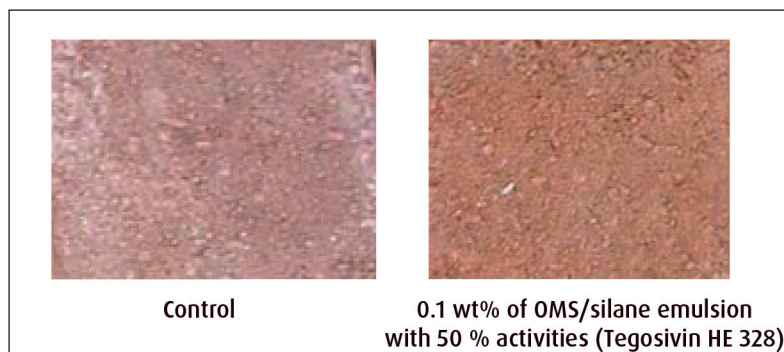


Figure 7: Primary efflorescence control, surface appearance of an OMS treated and non treated specimen

Long-lasting protection using the post application of water repellent depends on the penetration depth. Quite simply, the deeper the water repellent penetrates into the concrete the better and more durable the protection. With modern chemistry and technology, penetration depths of $> 10 \text{ mm}$ can be easily achieved. The penetration is influenced mainly by a variety of parameters such as the porosity of the concrete, the water/cement ratio, the nature of water repellent, the moisture content in the concrete, application method, consumption of the water repellent and alkalinity of the concrete [2].

For centuries, metal soaps (oleates and stearates) have been used for integral protection of concrete and cement based materials against the capillary water uptake. This is a relatively successful method of avoiding problems in achieving high penetration. The biggest drawback of these water repellents is their lack of durability and the negative influence on the physical properties of the fresh and hardened concrete. Metal soaps will be washed out over time and in many cases the air content of the concrete is increased which leads to a lower compressive strength of the hardened concrete [3].

In recent years, new waterborne chemicals based on a combination waterborne, organo-modified siloxanes (OMS) and silanes have come on the market. Their unique chemical structure makes these materials very efficient. The recipe for success for these silicone-based water repellents is the low dosage level, no significant influence on the concrete properties and excellent reduction in water absorption. Due to the reduced capillary water uptake, primary and secondary efflorescence and freeze thaw damage are reduced to a minimum. The per-

meation of dissolved salts such as sodium chloride is also greatly reduced. This protects the concrete against damage caused by rebar corrosion.

The main application areas for OMS-based water repellents are in efflorescence control or as water repellents in manufactured concrete products such as pavers, tubes or any other concrete products that come into contact with moisture. These OMS-type products have recently also been used for concrete materials with water-resisting properties according to EN 934-2.

Silicone chemistry

Among all the different kinds of hydrophobic products developed for the building industry, silicone resins, silanes, oligomeric and polymeric siloxanes have proven to perform best in protecting masonry façades from water penetration and environmental influences. *Figure 4* illustrates how they are manufactured. In the construction industry, alkyltrialkoxysilanes such as isobutyltriethoxysilane, n-octyltriethoxysilane and iso-octyltriethoxysilanes are highly suitable for hydrophobization purposes. Longer alkyl chains provide steric protection to the Si-O bond. Due to their lower reactivity, silanes can achieve penetration depth even in alkaline substrates. They undergo condensation reactions and crosslink and eliminate alcohol after application to the substrate. On inert surfaces, this reaction often needs the presence of a catalyst system.

Siloxanes and silicone oils are oligomeric or polymeric molecules based on Si-O-Si chains. Because of their low intermolecular forces, these oils are liquid over a wide temperature range even at a high molecular weight. In organo-modified siloxanes, some of the methyl groups at the silicon atoms are substituted by other organic groups. Organo-modified siloxanes are mainly used in construction applications for hydrophobization of inert and natural substrates or as raw material for antifoams. They are also suitable for the treatment of aged concrete that, due to carbonation, has a reduced pH value. The main applications for these products are façade treatment and protection against rising damp. The higher reactivity of siloxanes compared to that of monomeric silanes means that they do not need a catalyst for curing. On high alkaline substrates, the curing process of siloxane is so fast that it does not allow the molecule to penetrate very deep into the substrate.

Waterbased, solvent-free emulsions based on OMS and silane chemistry are suitable as they can be easily blended into the concrete matrix. The addition of the emulsion to the mixing water gives a very homogenous distribution of the silicone materials.

All silane/siloxane-based compounds carry hydrophobic alkyl chains and hydrophilic Si-O-R groups (with R = methyl, or ethyl). The hydrophobicity mainly depends on the length of the alkyl group. Longer alkyl chains give also good resistance against alkalinity as they set up a sterical shield for the Si-O-Si bonds which are prone to hydrolysis. When applied to the substrate, the alkoxy groups of these products react with water or humidity to form a non-stable silanol intermediate which will spontaneously polycondensate to form a hydrophobising film (*Figure 6*). At the time, the reactive OH-groups from the silanols can form irreversible bonds with the mineral substrate.

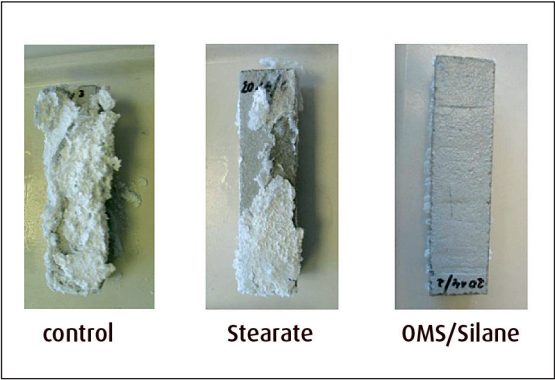


Figure 8: Secondary efflorescence control, surface observation of samples treated with different water repellents (after 7 days storage)

These can be regarded as an anchorage system between the hydrophobic film and the building substrate. Hence, by treatment with silicone compounds the building material becomes hydrophobized through a chemical modification and newly formed bonds. The performance and durability of the water-repelling treatment depends on the penetration depth of the silicone material and the active content of the applied product.

Visual testing of efflorescence

Dosages of 0.05 to 0.1 wt% of silicone actives, based on the cement weight, are usually sufficient to avoid primary and secondary efflorescence on manufactured concrete products. This low amount of silicones is sufficient to interrupt the salt transport in the pores. Due to the high reactivity of the OMS in alkaline areas, a rapid protection against salt blooming within in the first 24 hours can be achieved.

Testing primary efflorescence under laboratory conditions is limited to visual testing 24 hours after the concrete casting. Colour fading is easy to see without any high-tech equipment and can also be used to measure the different colour intensities (see *Figure 7*).

Secondary efflorescence can be tested according to DIN 52111. The concrete is stored for 28 days at standard climate conditions. The specimen is partly placed (approx. 1 cm) in a sodium sulphate solution (100 g sodium sulphate/900 g water). The sample's surface is checked

Figure 9: Specific requirements for water resisting admixtures (at equal w/c ratio)

No	Property	Reference Mortar/concrete	Test method	Requirements
1	Capillary absorption	EN 480-1 mortar	EN 480-5	Tested for 7 days after 7 days curing: test mix ≤ 50 % by mass of control mix Tested for 28 days after 90 days curing: test mix ≤ 60 % by mass of control mix
2	Compressive strenght	EN 480-1 reference concrete I	prEN 12390-3:1999	At 28 days: test mix ≥ 85 % of control mix
3	Air content in fresh concrete	EN 480-1 reference concrete I	EN 12350-7	Test mix ≤ 2 % by volume above control mix unless otherwise stated by the manufacturer

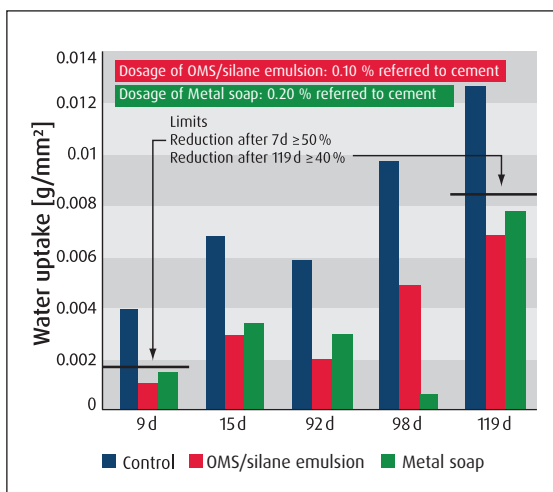


Figure 10: Water uptake according to EN 480-5

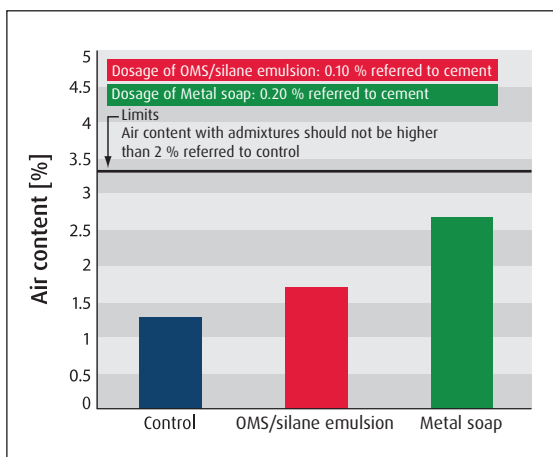


Figure 12: Influence of water repellents on the air content (%) of concrete

for crystallized salts after one day, three days and seven days. Depending on the sample's porosity, efflorescence may be observed already after a few hours or only after some days. An example is shown in Figure 8.

According to EN 934-2, water-resisting admixtures for concrete, mortar and grouts are used to protect the concrete against capillary water uptake arising from rain, flowing water, rising damp etc. Manufactured concrete products, such as paving stones, concrete roofing tiles, or pre-cast concrete need long-lasting protection. OMS/silane based emulsions are very effective against the water permeation and are very durable due to the chemical reaction of the silicone molecule with the concrete matrix. Concrete is not affected or weakened by the addition of these products. Standard metal soaps are not very durable, because they are washed out over time. In addition, stearates, which are also widely used, might have a significant impact on the physical properties of the concrete such as compressive strength and air content. The necessary tests for certification (see Figure 9) have been carried out with a commercially available OMS/silane based emulsion. Figures 10-12 show the results compared to a control sample and a sample treated with metal soap.

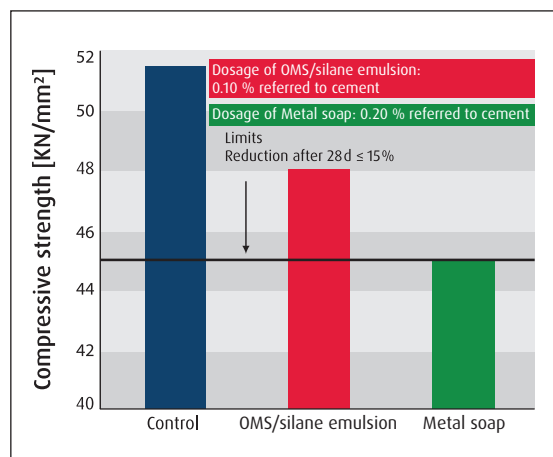


Figure 11: Variation in compressive strength of concrete when using different water repellents

Low water uptake and higher compressive strength

To fulfil the requirements as a water-resisting admixture, the water repellent should be easy to dose and be homogeneously distributed in the concrete matrix. A dose rate of approx. 0.1 wt% of a 50 % active OMS/silane emulsion based on the cement weight is sufficient to achieve the necessary protection. Despite the lower dosage of Si-based products compared to, for example, metal soaps, the results show excellent water reduction, indicated by the low water uptake.

The use of metal soaps as water repellents greatly reduces the compressive strength of concrete, (see Figure 11). A minor failure during concrete production could lead to huge problems, as the compressive strength could be lower than the required values. The result would be that the manufactured concrete would not receive the necessary CE-label.

In contrast, using the OMS/silane emulsion technology gives higher compressive strength values and thus reduces more room for production failures. The most likely reason for losing compressive strength is air content. It is well known that different types of cement negatively influence this. This means the air content is higher than usual. Metal soaps are known to act like air entrainers. If circumstances are non-ideal the air content could be too high and the concrete would then be out of specification. If metal soaps are to be used, the correct cement has to be chosen for use with it or an additional defoamer has to be added. OMS/siloxane emulsions have no significant influence on the air content. The air content is untouched which means a broader range of cement types can be used. ◀

References

- [1] Schueremans L., van Gemert D., Proceedings of Hydrophobe II conference, September 1998
- [2] Fliedner C., Silane as "Water Repellents for Concrete" part 1 and 2, in Bautenschutz und Bausanierung, 1994
- [3] Quadrelli M., Roos M., König F., et al, New powderous water repellents for dry mortar applications at idmmc one, 2007