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THE EFFECTIVENESS OF SILANE COATING IN PREVENTING WATER INTRUSION AND CHLORIDE PENETRATION

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OBJECTIVE

The objective of this report is to evaluate the effectiveness of silane coating (isobutyltriethoxy silane) to prevent water intrusion and chloride penetration.

SCOPE

This work involved the treatment of mortar (made from GP cement) with commercially available Dry-Treat 100N. This product contains almost 100% of isobutyltriethoxy silane as an active component (less than 1% ethanol). The properties being evaluated and investigated were water absorption, water-vapour transmission, drying shrinkage, and chloride penetration. Some of test methods which are not covered in the standards (ASTM and Australia Standard) were adopted and modified from the literature reviewed.

INTRODUCTION

The rapid deterioration of various reinforced concrete structures has been a widely recognised problem. This can be attributed to the ingress of moisture, oxygen, and chloride ions to the concrete/steel interface and the loss of alkalinity due to absorption of carbon dioxide from the atmosphere. These destroy the passivity of the reinforcing steel and result in corrosion. The formation of rust gradually results in an increase in volume compared with the original steel so that swelling pressure will cause cracking and spalling of the concrete. To prevent the rapid deterioration, the penetration of these destructive agents has to be retarded or stopped entirely. Some methods to prevent this rapid deterioration occurring are cathodic protection, adequate concrete cover over the metal reinforcement, correct placement practices, and appropriate mix design. For both new and pre-existing structures, protective coating is the other alternative. There are various protective coatings commercially available which fill the capillary pores or coat the capillary pore walls. Protective coatings can also provide protection against alkali-aggregate reaction (AAR) and sulphate attack which other methods may not provide. One of these protective coatings is generically known as silane.
This short report is going to look into this particular protective coating. First, commercially available different types of protective coatings are going to review briefly. Then some properties of silane are discussed. Finally, the experimental results and conclusion are presented.

BRIEF LITERATURE REVIEW

TYPES OF COATINGS

A wide range of coatings for concrete is available. Coatings used to inhibit reinforcement corrosion may be categorised into three groups[1,2]:

Water repellent coatings

Water repellent coatings are non-film-forming coatings. They cause the surface of the concrete to become hydrophobic. The coatings are clear and so do not change the appearance of the concrete. Included in this type of coating are silicone compounds, silane, and siloxane (partially polymerised silanes). Their penetrability relies on low molecular weight, hence small molecules, to line the voids and capillaries in the concrete. There the molecules polymerise to form polymer. Siloxane, for example, being a larger molecule than silane, is not as penetrable as silane. Siloxane, however, is less volatile. Larger molecules still are the silicone resins which are basically a superficial surface treatment. More about silanes will be discussed later.

Membrane coatings-flexible

These coatings are commonly high build pigmented films which provide continuous impervious barriers to further ingress of contaminants (water, water vapour, chlorides and CO_2). They can bridge small existing cracks and, to a certain degree, cracks that may appear later (due to their high elongation combined with their thickness). Such coatings include acrylic, polyurethane, and epoxy. In contrast to water repellent coatings, this type of coating depends on a pinhole free surface. The main disadvantage of this type of coating is the application cost and difficulty to obtain pinhole free membrane. In addition, when a membrane coating is breached, the coating will slow down moisture escaping from damp concrete.

Non-flexible coatings

These type of coatings are similar to the flexible membrane coatings providing a physical barrier against corrosive agents. They are applied where there is little risk of cracking on the structure. Polyurethane, polyester epoxy, and catalysed acrylics are some examples of this category.

PROPERTIES OF SILANES

Silane is a common name for the product of the reaction between alkyltrichlorosilane and alcohols. Most silane-based sealers are mixed with alcohol as solvent carrier to help in penetration of relatively dry concrete. Pure/undiluted silanes are often called neat silanes.

Advantage:

- ⇒ Good penetration and excellent water-vapour transmission to allow escape of internal moisture. Deep penetration into the concretes protects the sealer from weathering degradation. In comparison, membrane coatings stay on the surface and may be subject to extreme weather and UV attack. Thus, this can lead to blisters, cracks or peeling of the protective coating. Moreover, membrane coatings block the pores which may cause spalling due to internal vapour pressure.

⇒ Good durability and strong chemical bond.
⇒ They do not require the substrate to be free from surface imperfections which would hinder the effectiveness of membrane coatings.
⇒ A transparent appearance with no change in colour or texture of the treated surface.

Disadvantages :

⇒ Difficulty to determine if the repellent has been applied uniformly and effectively over all surface.

It is still arguable whether silane sealer reduces the resistance to freezing and thawing.

Table 1 taken from *Bartlet*[1] provides a relative comparison between silanes and siloxanes.

Table 1 Typical commercial silane/siloxane water repellents

Material	Penetration depth (mm)	Advantages and limitations
Silane		
Isobutyl tri ethoxy silane	5	High cost because of considerable loss due to volatility. Preferred for maximum protection. Use neat or typically diluted to 40% in ethanol
Iso-octyl trimethoxy silane	3-4	Lower volatility than iso-butyl silane and thus less costly.
Silane/siloxanes mixture		
Iso-octyl trimethoxy silane/oligomeric iso-octyl trimethoxy siloxanes in hydrocarbon solvent	3-4	Moderate cost, general purpose product, some moisture acceptable, more tolerant of application in warm or windy weather. Typically 25% solution.
Siloxanes		
Oligomeric trimethoxy siloxane in hydrocarbon solvent	1-3	Moderate cost and some moisture acceptable, avoids volatility problems of low molecular weight materials but lacks penetration. Typically 5% solution.

Mechanism

The mechanism through which the alkyl alkoxy silane improves waterproofing can be explained by two-step chemical reactions between the silane and the concrete surface[1,3] (see fig.1)

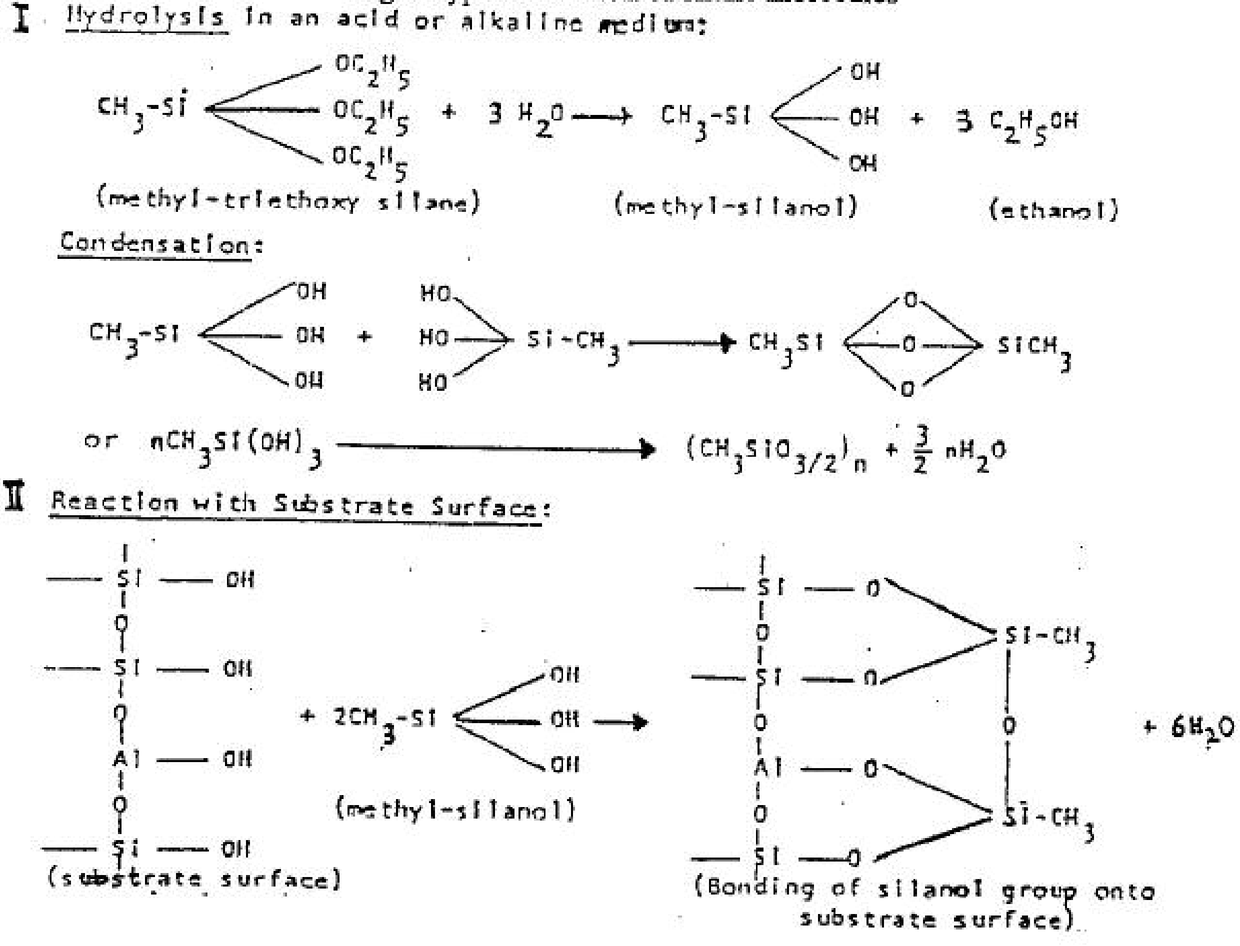
Step 1: hydrolysis in an alkaline medium based on cement hydration.
Step 2: reaction between silanol groups (-SiOH) and hydroxyl groups (-OH) on the concrete surface.

-SiR groups are non-polar and impart hydrophobicity to the concrete surface. As the alkyl group gets larger, losses due to evaporation and hydrolysis become negligible. During application, there are at least 3 simultaneous processes occurring. They are in decreasing order of speed[4]:

1) The sealer liquid is sucked into the substrate by capillary action. Smaller pores absorb more strongly, but they hold less sealer liquid. Large pores behave otherwise.
2) The reactive site(s) of the treating agent molecule reacts with the substrate and /or with neighbouring molecules. The two chemical reactions above show that the availability of water for reaction with silane is crucial. For example, one litre of isobutyltriethoxy silane requires 216 gram of water. This can be adequately provided through adsorption and/or absorption of moisture in the atmosphere.
3) Treating agent evaporates.

If the sealer is applied under unfavourable conditions, such as low humidity or high wind, evaporation may take place faster.

Fig.1 Typical reaction of silane molecules



$CH_3-Si(OC_2H_5)_3 + 3H_2O \rightarrow CH_3-Si(OH)_3 + 3C_2H_5OH$

$nCH_3Si(OH)_3 \longrightarrow (CH_3SiO_{3/2})_n + \frac{3}{2}nH_2O$

What other investigators have found:

- As concentration of the active silane increases, both penetration depth and overall water-proofing performance also increase. Silane needs not be diluted in alcohol to promote penetration[5].
- Existing silane treated surfaces can easily absorb many more applications of silane sealer, and the new coat often penetrates deeper into the concrete.
- High quality concretes can be significantly improved, but low quality ones (or high w/c ratio) may be more effectively sealed by membrane coatings. Lower w/c ratios give better waterproofing performance and deeper penetration depth. These are due to the very low viscosity of the silanes and lesser amount of surface area of the internal void space available to be sealed in high grade concrete. *Paul* [5] had compared the waterproofing performance of 0.5 W/C ratio against 0.7 w/c ratio.
- The best time for sealing is when the concrete is relatively new and before significant exposure to chloride. Once the water level in concrete is high, water repellents may have little use.
- Water-proofing performance (and penetration depth) is directly proportional to cumulative amount of silane applied and inversely proportional to moisture content and permeable void of the concretes.
- Time needed to achieve desired coverage rate increases slightly as the number of pre-treatments increases. The vapour transmission is relatively high compared to other type of coatings. It was also found that the pore size distribution and total pore volume of a treated concrete are almost the same as those of untreated concrete[6]. This proves that the sealer does not plug the concrete pores but merely coats the interior wall of the capillaries.
- The ability of silane to penetrate is less affected by the presence of moisture in comparison to the more economical siloxane sealers.
- *Wong et al* reported that silane treatment on 0.45 and 0.50 w/c ratio concretes does not have any significant effect on the corrosion current. Also, alkyl-alkoxy silane treatment concrete is effective in reducing the rate of corrosion of reinforcing steel. The rate was reduced by a factor between about 14 to 50,000[3].
- It was thought that the treated concretes would perform better on long term if the service conditions gave opportunity for any absorbed moisture to rediffuse out[1]. Unlike membrane coating treatment, silane coating treatment allows absorbed moisture to rediffuse out when the concrete is not longer submerged under water.
- It is still debatable whether silane and siloxane may actually promote carbonation due to ready access of CO_2 to the dry capillaries.

EXPERIMENTAL METHOD

Mortar was chosen instead of concrete in order to reduce variation due to aggregate. Variation was further reduced by not using any admixtures in the mortar. The mortar was proportioned to have relatively high permeability. Mixing of the mortar was in accordance with ASTM C 305 - 94 "Mechanical mixing of hydraulic cement pastes and mortars of plastic consistency". Cylinders and drying shrinkage specimens were cast.

Table 1 Constituents of the mortar used

Material	Density (kg/m^3)	SSD (kg)
GP cement	3150	3.41
fine sand	2650	10.73
water	1000	1.73

Water-to-cement ratio = 0.51
Sand-to-cement ratio = 3.15
Flow (mm) = 110±15 mm
Sand absorption = 1.95%
Compressive strength (predicted from preliminary work) = about 20 MPa at 28 days

To ensure proper compaction, continuous vibration and tamping with steel rod were applied. The mortar was placed roughly on 2 layers. Cylinders of 75 mm diameter, 150 mm height were used for absorption and water-vapour transmission and 100 mm diameter, 200 mm height ones for chloride penetration.

Experimental procedures and methods were adopted from the ASTM or Australian Standard whenever applicable and, if not, they were adopted and modified from literature reviewed[7].

Water absorption

Absorption specimens were air-cured at 23°C with relative humidity about 50% until the age of 7 days. Then they were oven-dried at 100°C for 24 hours and allowed to cool to room temperature. After that, the cylinders were coated with Dry-treat 100N by dipping method. They were dipped for about 5 seconds. The application rate was determined by weighing the amount of silane liquid absorbed on known surface area. Two coats were applied with 6 hours in between as recommended by the supplier. Control specimens were also oven-dried and allowed to cool to room temperature before immersion. Initial weights of all specimens were recorded prior to immersion in water at (23±2)°C. Weight changes were monitored at time intervals. Cylinders were removed from water one at a time, surface dried and weighed. This method was used to compare the relative percentage of water absorption between surface-treated and untreated specimens. After a period of time, the water absorption process was reversed to water-vapour transmission in the condition as described below (reversed cycle).

Water-vapour transmission

This experiment was to evaluate the effect silane treatment might have on the rate of moisture loss from mortar. The water-vapour transmission specimens were cured in the same manner as the absorption ones. After curing 7 days, these cylinders were soaked in water for 24 hours. Cylinders to be coated were then removed and the surface allowed to dry prior to coating in the standard laboratory condition. Two coats was applied. The application rate was also noted for comparison purposes later. Specimens were weighed and put in the oven at 40±1°C. Again, the weighed changes were monitored at regular intervals. Similarly, after a period of time, the water-vapour transmission process was reversed to water absorption in the condition as described above (reversed cycle).

Drying shrinkage

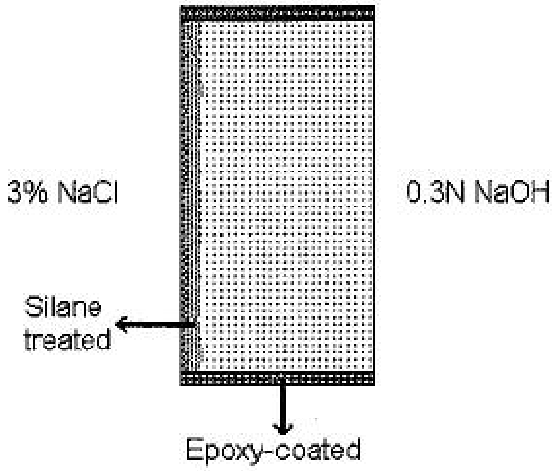
Drying shrinkage prisms were prepared as outlined in ASTM C 596-*89 "Drying shrinkage of mortar containing Portland cement*". After curing in saturated limewater for 72 hours, all the prims were removed and wiped dry. The prisms to be coated with silane were left surface-dry in the standard laboratory condition and only one coat was applied. Then all prisms were placed in the laboratory according to the standard and shrinkage measurements were made over a period of time.

Chloride penetration

Two methods were used to study the water-soluble chloride penetrability. For these methods, 100 mm diameter, 50 mm height discs were cut from the cylinders.

1. ASTM C 1202 "Electrical indication of concrete's ability to resist chloride ion penetration"
   All specimens were prepared and preconditioned as outlined in the standard. They consisted of two specimens without silane coating and a number of samples with differing numbers of coats on one of the flat surfaces. The coated surface was subjected to the sodium chloride solution prescribed in the standard, while the uncoated surface was subjected to the sodium hydroxide (see Figure 1). A modified test was conducted on one specimen without silane coating in which the specified solutions at both ends were replaced by distilled water.

Figure 1 Specimen for ASTM C 1202 test



2. 28-Days ponding test
   The specimens for this test consisted of one control disc and one disc with 3 coats of silane (at the age of 14 days). The specimens were epoxy-coated on the side and on only one flat end of the discs. Then at the age of 14 days they were partially immersed, uncoated end down, in 3% by weight NaCl for 28 days. At the end of 28 days, mortar powders for certain depths were collected by drilling and analysed for water soluble chloride ion concentration.

Penetration depth
At the end of the accelerated chloride measurement test (ASTM C 1202), the cylinder specimens were split in half. After wetting, the depth of the dry layer (due to the presence of silane) of the two cross sections was measured to the nearest millimetre. Four measurements about equal spacing were taken for each cross section (hence 8 measurements altogether) and their average was taken as nominal penetration depth.

Moisture content
During preconditioning as prescribed by ASTM C 1202, some of the specimens' weights were recorded (weight before preconditioning, weight after preconditioning, and dry weight).

RESULTS AND DISCUSSION

Water absorption and water-vapour transmission
The results for both the initially water absorption and the water-vapour transmission tests (followed by their respective reversed cycles) are plotted on Figure 2 and Figure 3. It was found the results from all specimens in each test were very consistent.
Both figures show the same trend. There was significant resistant to water penetration (absorption) when the specimens were immersed in water. Hence, the coating is expected to resist water soluble chloride ion ingress.

The water-vapour transmission of the coated specimens, however, was not significantly lower than the control. In other word, the coating had good breathablity. This is advantageous since the already diffused chloride ions will not diffuse any further into the mortar when the specimen undergoes drying. They could perhaps withdraw slightly with the escape of moisture from mortar during this period. Furthermore, for chloride ion ingress to advance in subsequent immersions, water has to start penetrating the mortar again. So the coating will retard the penetration of the water soluble chloride ions.

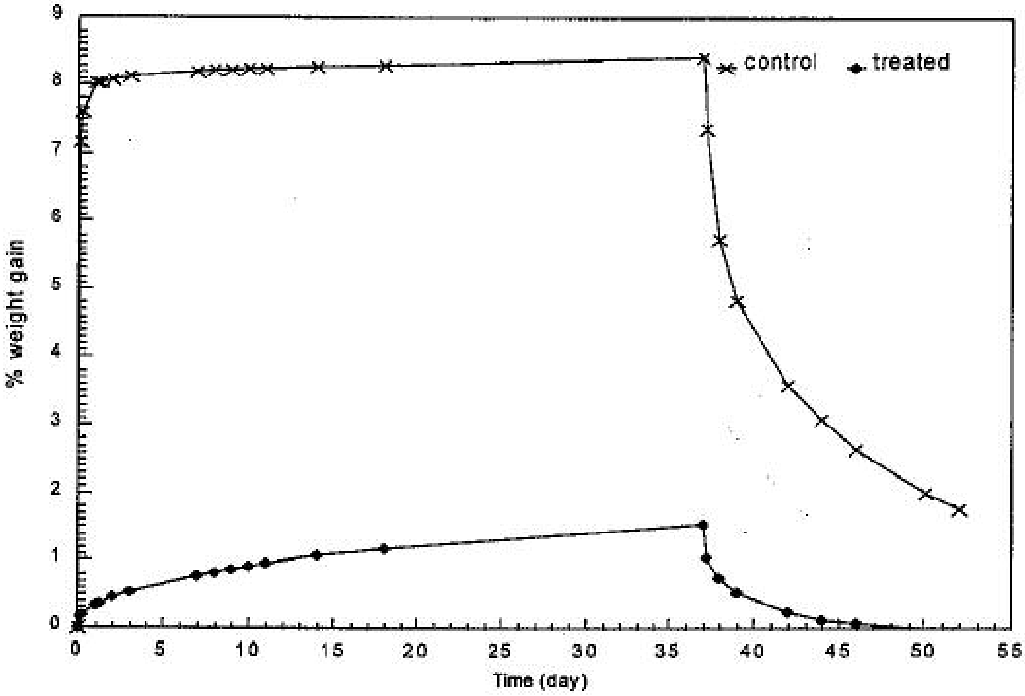


Figure 2 - The specimens initially underwent water absorption, and then followed by water-vapour transmission (oven drying at 40 degree Celsius).

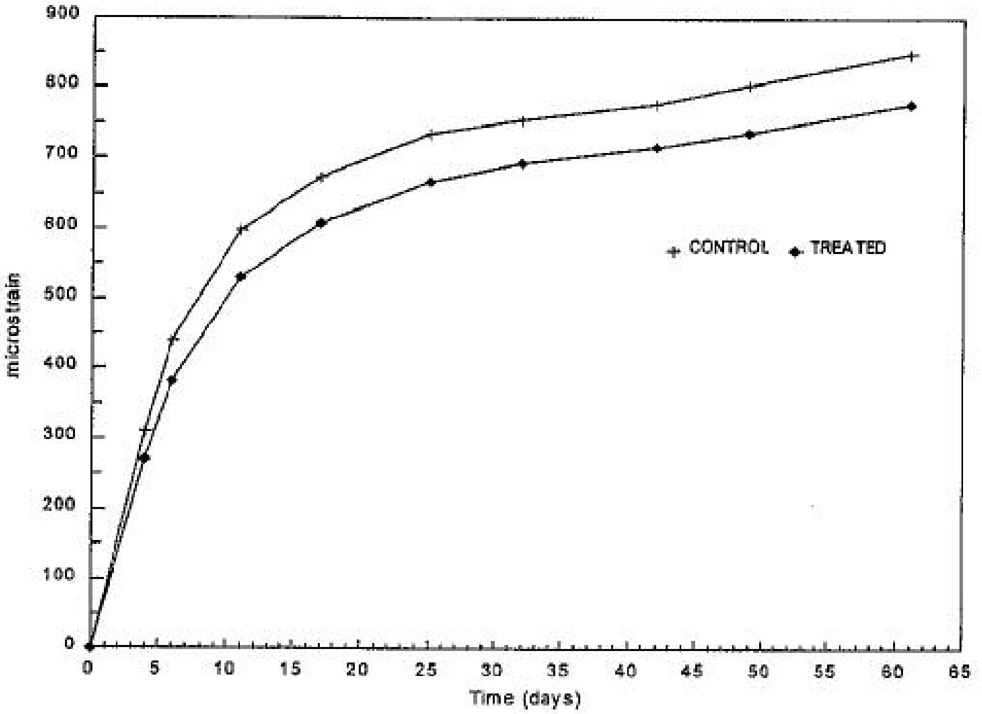


Figure 4 - Drying shrinkage of treated and control specimens

Chloride penetration and penetration depth

Table 2 - Classification of charge transfer data for concrete

Charge passed (Coulombs)	Chloride permeability
> 4000	High
2000 - 4000	Moderate
1000 - 2000	Low
100 - 1000	Very low
<100	Negligible

Table 3 - Summary of results from ASTM C1202 test

		3A	0C	2A	2B	1A	1B	0A	OB
Coulomb passed		624	340	1933	1216	4369	2919	3733	4409
Age (days)		14	14	13	13	8	12	9	8
Silane penetration depth (mm)		10	0	10	9	9	11	0	0
Application rate (lit/m^2)	1st coat	0.22	0	0.22	0.22	0.24	0.30	0	0
	2nd coat	0.21		0.21	0.22				
	3rd coat	0.22							

Note: Prefix number indicates the number of coatings applied and the letter designates the specimen.

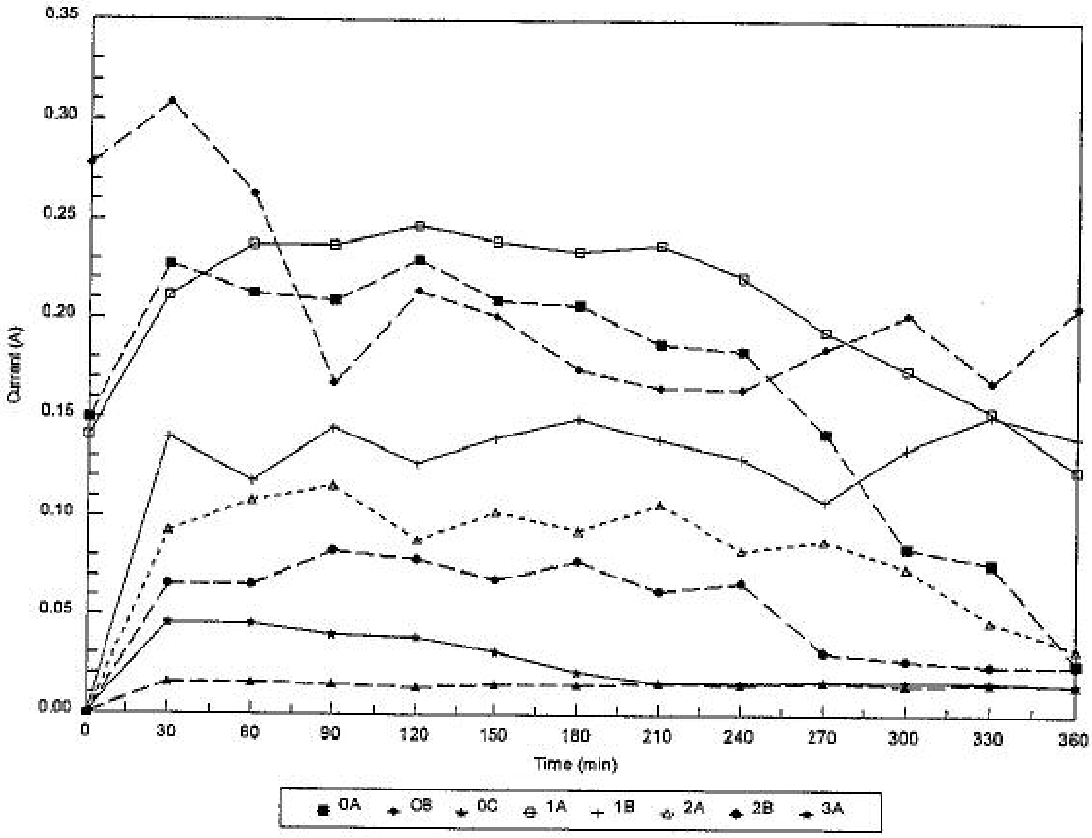


Figure 5 - Current as a function of time: electrical indication of mortar's ability to resist penetration of water-soluble chloride ion

Table 4 - Concentration of water soluble chloride (%)

	Drilling depth (mm)				Test performed
Specimen	3 mm	7 mm	15 mm	25 mm	
1B	0.310	0.295	0.235	0.060	ASTM C 1202
0C	0.250	0.075	0.005	0.005	ASTM C 1202
3A	0.055	0.085	0.010	0.005	ASTM C 1202
0D	0.580	0.300	0.205	0.105	28-day ponding in 3%NaCl
3B	0.010	0.005	0.005	0.005	28-day ponding in 3%NaCl

1. ASTM C 1202 test did not indicate satisfactorily the performance of the silane coating to resist penetration of water-soluble chloride ion (see Table 3). Despite similar age, the Coulomb passed for 1A and 0B were not much different. Again for similar age, the Coulomb passed for 2A and 2B were significantly different. Moreover, the results of 0C and 3A showed that the untreated specimen performed better than the treated one.
2. The age of specimens played a significant role in the chloride resistance, especially early age, since hydration reaction took place at an exponential rate. The coulomb passed decreased as the age of the specimen increased. The chloride permeability indication changed from high (greater than 4000 Coulomb) to very low (100 to 1000 Coulomb).

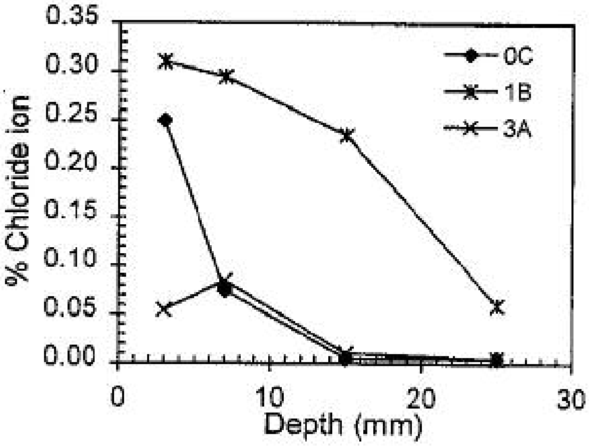


Figure 6 - Chloride profile for some of the accelerated test specimens

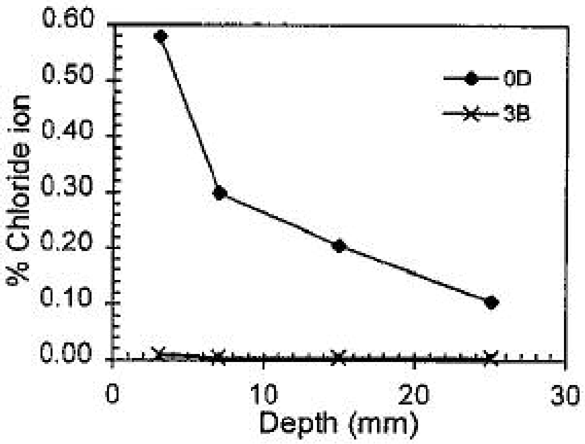


Figure 7 - Chloride profile for 28-days ponding test specimens

3. The penetration depth of silane seemed to be independent of the number of coatings applied and application rate.
4. As mentioned previously, the penetration depth of silane coating on concrete has been reported in the range of 1 to 5mm. Silane molecule was found to penetrate deeper into the mortar used in this experiment (9-15 mm).
5. The chloride profile for 28-day ponding test (see Figure 6) shows clearly that silane coating can resist water soluble chloride ion. When the chloride profile for 0E is extrapolated to achieve 0.005% Cl (similar to that of 3B), the depth will be about 35 mm. Therefore, 10 mm silane penetration is equivalent to 35 mm additional cover.
6. Except for the first depth, the chloride profile for accelerated test (0C and 3A, Figure 6) is quite similar. Hence, the 60 volt potential difference applied had driven the water-soluble chloride ions deeper into the mortar. The mechanism in which this occurred is unknown. Compared 0C (accelerated test) and 0D (28-day ponding test), both show similar trend of chloride profile. However, the chloride profile for 0C is much lower than for 0D.

Moisture content

Preconditioning as prescribed in ASTM C 1202 increased the moisture content of the control specimen by 12.7%. However, the same preconditioning increased the moisture content of the treated specimen only by 1.2%. The latter result may not be very accurate since under vacuum some silane may have been vaporised.

Compressive strength

Control specimens = 17.5 MPa (at 60 days)
Treated specimens = 11.0 MPa (at 60 days)

Control cylinders had higher compressive strength since during testing they were moist cured at the same time.

RECOMMENDATION

It is not known to what extent the presence of silane in the mortar will affect the drying shrinkage on small dimension specimen. Hence, for similar investigation it is recommended to use larger dimension of specimen.
It was found that the performance indicator based on ASTM C1202 alone was not reliable and varied greatly with age. This test restricted the number of test could be performed in one day (2 or 3 specimens maximum). Therefore, the age factor may be minimised if the test is conducted at later age (eg. 28 days) and other test method should be used if there is a large number of specimens to be tested.
Moisture content of specimen determines greatly the penetration depth of silane molecules. The development of strength of mortar may be affected to some extent by silane treatment.

CONCLUSION

1. Silane coating, Dry-Treat 100N, could significantly reduce water absorption and water-soluble chloride ions. It also had an excellent water-vapour transmission. For these two properties combined, it can be expected to retard reinforcement corrosion and hence prolong the service life of a structure. From the 28-day ponding test, application of silane with penetration depth of 10 mm was found equivalent to about 35 mm mortar cover.
2. Due to its excellent water-vapour transmission, the coating had little effect on the drying shrinkage of the mortar.
3. Penetration depth of silane depended on the moisture condition of the specimen. Silane molecules penetrated much deeper into drier specimen. The penetration depth of silane, however, seemed to be independent on number of coatings applied and application rate. Silane penetrated into mortar between 9 to 15 mm.
4. ASTM C 1202 (accelerated test) alone did not indicate the performance of the silane coating satisfactorily. Ponding test should be used to confirm the interpretation of the result.

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