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Ethyl silicate for surface treatment of concrete – Part II: Characteristics and performance

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ABSTRACT

In this study, several aspects of the surface treatment of concrete with ethyl silicate were investigated. After the treatment, two different types of concrete (w/c 0.45 and 0.65) showed a dramatic decrease in capillary suction, chloride diffusion coefficient and carbonation depth. A penetration depth into the concrete of about 3–5 mm was assessed. Microstructural investigations showed evidence of a chemical interaction of the amorphous silica gel within the concrete forming calcium silica gel and a selective distribution of silica gel, which was mainly deposited in the small pores. In addition, the brightness and colour changes of the concrete surfaces after the treatment were analyzed quantitatively, finding limited differences, further decreasing over time. This last aspect is relevant for architectural applications of concrete, for example façades of residential buildings, where the architects may be interested in using the texture of concrete but are concerned by possible colour changes related to surface treatments application.

1. Introduction

1.1. Surface treatment of concrete

In reinforced concrete, the penetration of aggressive agents through the cover zone is critical for the reinforcement corrosion and hence for the durability of the concrete structure.

In old structures, the problem of durability used to be totally underestimated during construction, due to the scarce awareness of the degradation mechanisms and processes affecting reinforced concrete. This often led to unsuitably high water to cement ratio and small cover thickness, presently causing urgent repair works in such old concrete structures. Even in the cases when reinforcement has not started to corrode yet and the cover is still intact, the rebars may be threatened by incipient corrosion due to deep carbonation [1,2].

In new structures, a common strategy to delay carbonation and ingress of chlorides through the cover zone is decreasing the total porosity of the concrete, for example by decreasing its water to cement ratio. However, this strategy exhibits two main drawbacks: firstly, the protection could be insufficient in highly aggressive service environments (e.g. marine, industrial, etc.) and, secondly, the concrete is typically overdesigned everywhere in the structure, except for the cover zone. The required additional consumption of cement and admixtures could be avoided by selectively improving the quality of the cover zone, e.g. by an appropriate surface treatment. Of course, surface treatments should not be viewed as a basis for reducing cover or for inadequate mix design [1], but as a means for selectively enhancing the concrete properties near the interface with outdoor aggressive environments [3].

Hence, in order to increase the durability of new and existing concrete structures, several kinds of surface treatments have been proposed, mainly classified according to EN 1504-2:2004 [4] as *hydrophobic impregnation* (producing a water-repellent surface, with no pore filling effect), *impregnation* (reducing the surface porosity, with partial or total pore filling effect) and *coatings* (producing a continuous protective layer on the surface of concrete). Hydrophobic impregnation [5–7] is usually performed through silanes or siloxanes application and is aimed to prevent the water ingress into concrete and, hence, to slow down the decay processes, due to the fact that both chemical and physical–mechanical attack is very slow, or even negligible, in dry conditions. Impregnation and coatings are usually performed through organic polymers, aimed at creating a physical barrier against the ingress of aggressive

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agents responsible for the degradation of concrete and/or reinforcement, i.e. chloride and other soluble salts, CO_2, chemical agents and water itself. In both cases, the use of organic products gives rise to:

- durability concerns, as they quickly lose their initial properties in outdoor environments, due to their sensitivity to UV, oxygen, temperature, humidity, pollutants, etc. For example, reduced efficiency of hydrophobic properties of silanes–siloxanes–polysiloxanes after about 5 years has been reported [8], hence the surface treatment should be repeated quite often;
- compatibility concerns, especially when continuous coatings or pore-blocking sealers are used. In such cases, the transport of water vapour is almost reduced to zero and water trapped behind the protective surface layer may cause its detachment.

In order to increase the durability of surface treatments, the use of inorganic products has been proposed as well. These products are mainly aqueous solutions of sodium silicate, also known as "waterglass", and, to a much lower extent, potassium silicates and fluosilicates [9]. These silicates, usually considered as pore-blockers, are supposed to react with portlandite to form C–S–H gel and NaOH [9] and to increase the performance of the impregnated layer, in terms of hardness and impermeability. However, the experimental data on the performance of sodium silicates for concrete impregnation are limited [5] and their mechanism in improving the concrete performance is still unclear [9]; moreover the possible increase in the risk of alkali-silica reaction due to the formation of NaOH as a by-product from the reaction with portlandite should be investigated. While some authors [5] report that sodium silicate minimally penetrates into concrete and is quite ineffective in preventing water absorption and chloride penetration, others report that its performance can be significantly improved by post-treatment with cationic surfactants (alkyl quaternary ammonium salts) [10].

In the present paper, the use of ethyl silicate, widely used for the consolidation of weathered stones in architectural restoration [11], for the surface treatment of concrete is investigated.

1.2. Ethyl silicate as a consolidant for stone

Ethyl silicate (ethyl ester of silicic acid – $Si(OC_2H_5)_4$ – often referred to as TEOS – tetraethylorthosilicate) is an alkoxysilane compound which is usually applied onto the stone surface by brushing or spraying, in solution with low viscosity organic solvents. Once penetrated into the pores, it undergoes a two-stage curing process: firstly hydrolysis, giving silanol and ethanol, and secondly dehydration/condensation of silanol, leading to the precipitation of amorphous silica gel inside the stone pores [12]. In silicate-rich stones, e.g. sandstones, silanol binds to the hydroxyl groups present in the silicate phases, thus leading to an appreciable increase in cohesion and mechanical strength [13]. On the contrary, in carbonate stones, e.g. marble, the ethyl silicate hardening simply results in a pore-filling effect, with limited re-adhesion and consolidation effects [14].

The reasons for the wide use of ethyl silicate for stone consolidation are mainly its small monomer size and low viscosity, leading to deep penetration into the stone, and its hardening by-products (ethanol and water), which are volatile and do not damage the stone. Moreover, the final reaction product of TEOS is silica gel, which exhibits good compatibility with stone and good durability, unlike many polymeric consolidants [8]. The incomplete reduction of open porosity (which allows transport of water vapour) of stone and the absence of an abrupt interruption between the impregnated and the untreated zones [13] are further advantages of this consolidant.

1.3. Applications of TEOS to concrete

The application of TEOS to concrete is expected to take advantage of the same features largely exploited for stone consolidation, i.e. good penetration depth, good chemical–physical–mechanical compatibility, high durability of the final product (silica) and absence of the pore-blocking effect. This last aspect is very important for a satisfactory durability of the surface treatment, because the possible presence of water trapped behind the consolidated layer (e.g. from infiltration) might lead to its detachment, especially in case of freeze–thaw cycles. Moreover, the concrete impregnation with TEOS is expected to take advantage of the pozzolanic behaviour of ethyl silicate, which is based on the production of amorphous silica during the TEOS sol–gel process and which was assessed in the first part of the paper [15]; the formation of C–S–H is expected to improve the compatibility of the treatment with concrete and its final performance.

2. Materials

2.1. Concrete

Two concrete mixtures based on ordinary Portland cement (CEM I 42.5N), with water to cement ratio (w/c) 0.45 and 0.65 respectively, were prepared (Table 1) and concrete cubes of size $150 \times 150 \times 150\ mm^3$ were manufactured. The samples were cured for 4 months at $T = 20 \pm 1$ °C and $90 \pm 5\%$ RH.

2.2. Ethyl silicate

The characteristics of the ethyl silicate (Estel 1000, CTS, Italy) used for surface treatment of concrete are reported in Table 2. The solvent, white spirit, is a mixture of saturated aliphatic and alicyclic hydrocarbons denatured with dichloropropane.

2.3. Samples

After the 4 months curing, three $150 \times 150 \times 50\ mm^3$ prisms were obtained from each cube by cutting: one external prism was treated with TEOS on one face according to the procedure described in Section 2.4, the other prism was left untreated for comparison and the inner prism (certainly not carbonated) was cut into $20 \times 20 \times 20\ mm^3$ cubic samples for microstructure characterization.

2.4. Surface treatment and curing

In order to ensure constant moisture content throughout the sample and a good penetration of ethyl silicate into concrete, a preconditioning of the samples was carried out. As a matter of fact, materials in equilibrium with an environmental relative humidity and temperature around 40% and 20 °C, respectively, are recommended for a better outcome of the treatment [16]. Thus, the following procedure was adopted: the samples were dried at 50 °C for 48 h and then stored in a climatic chamber at $T = 20 \pm 1$ °C

Table 1
Mix design and properties of concrete.

	w/c 0.45	w/c 0.65
w/c	0.45	0.65
Cement content (kg/m^3)	330	275
Maximum aggregate size (mm)	32	32
Bulk density (kg/m^3)	2430	2362
Air content (vol.%)	2.0	2.5
Compressive strength at 28 d (MPa)	52.5	31.0

Table 2
Main chemical–physical characteristics of ethyl silicate Estel 1000 [16].

Active ingredient	Tetraethyl orthosilicate
Content of active ingredient (wt.%)	75
Solvent	White spirit
Catalyst	Dibutyltin dilaurate (DBTL)
Viscosity at 20 °C (cp)	4.9
Density at 20 °C (kg/l)	0.98
Dry residual (wt.%)	Minimum 35
Flashpoint (°C)	21–55
Boiling point (°C)	145–200
Appearance	Colourless liquid
Solubility in water	Insoluble
Risk phrases (Directive 2001/59/EC)	Ethyl silicate: Xn; R 20; R 36/37; R 10 Solvent: Xn; R 65; R 10 Catalyst: Xn + N; R 48/22; R 36/38; R 50/53
Safety phrases (Directive 2001/59/EC)	S 7/8; S 16; S 20/21; S 24–26; S 36–39; S 47; S 61

Table 3
Mean ethyl silicate consumption per unit area by brushing (slabs) and immersion (cubes).

Samples	Consumption (3 d brushing) (g/cm^2)	Consumption (24 h immersion) (g/cm^2)
w/c 0.45	0.06	0.02
w/c 0.65	0.10	0.03

and RH = 35 ± 5%, for 1 week. After a final weighing, the samples were ready to receive the surface treatment.

The product was applied by brushing wet on wet until rejection, only on one side of the samples; this was repeated three times, during three subsequent days.

At the end of the treatment the specimens were left under a ventilated hood ($T = 21 \pm 1$ °C; RH = 22 ± 5%) for about 1 week, in order to enhance the first and more substantial evaporation of the solvent. Thereafter, the samples were cured for a further 3 weeks in two different climatic chambers: at $T = 20 \pm 1$ °C and RH = 35 ± 5% and at $T = 20 \pm 1$ °C and RH = 90 ± 5%. These two curing conditions were chosen to assess the influence of relative humidity on the ethyl silicate's hardening process and on its interaction with concrete. The relevant samples were indicated as "w/c 0.45_35%", "w/c 0.45_90%", "w/c 0.65_35%" and "w/c 0.65_90%"; the suffixes "tr." and "untr." indicate respectively the presence or absence of the treatment.

From each 50 mm thick concrete prism, cylindrical cores ($d = 50$ mm) were obtained by wet coring. The cores were then dried at 50 °C for 48 h, to constant weight (maximum allowed deviation 0.1%). A two-component epoxy resin was then applied to the lateral surface of both treated and untreated cores, in order to seal it and exclude penetration of water or gas.

The cubic specimens ($20 \times 20 \times 20$ mm^3), after the same preconditioning described above, were treated with ethyl silicate by immersion for about 24 h. Their curing followed the same procedure previously described.

3. Methods

3.1. Mass variation during treatment and curing

The samples were weighed before the treatment and immediately after, as well as during the curing period, with an accuracy of 0.01 g, in order to monitor the evaporation of the solvent and of the TEOS hardening by-products.

3.2. Water sorptivity

The water sorptivity test (SN EN ISO 15148, EN 1062-3 and UNI 10859) was performed on treated and untreated cores by placing them on two plastic rods and keeping them immersed in 3–5 mm of deionized water.

Samples mass in surface-dry conditions was recorded after 4, 10, 30 min and 1, 2, 3, 6, 24 h.

At the end of the first water sorptivity test, in order to evaluate the penetration depth of ethyl silicate within the concrete, a layer of respectively 1, 2, 3 or 5 mm was cut from the treated side (previously immersed) of four samples; untreated samples were cut as well, for comparison. A second water sorptivity test was then performed on these sliced cores, after drying them at 50 °C for 48 h.

3.3. Chloride resistance

Two treated and two untreated samples were immersed in deionized water for 1 week to saturate them before starting the chloride resistance test. The rapid chloride migration test was performed according to Swiss standard SIA 262/1 [17] with a test duration of 24 h at an externally applied potential of 20 V leading to a chloride migration coefficient Dm (non-steady-state) calculated from the penetration depth of chlorides (colorimetric determination). During the test, one surface of the saturated test specimen (cores with diameter and length of 50 mm) is exposed to a 0.2 M potassium hydroxide solution without chlorides while the potassium hydroxide solution in contact with the second surface (the treated one, in the case of the treated samples) contains 3% NaCl.

After the voltage application, in which the temperature of the two solutions and the current were regularly measured, the cores were split in two halves and fluorescein and silver nitrate solution (Fixanal, Fluka) were sprayed on the freshly broken surfaces. The samples were then dried in an oven at 50 °C for 24 h in order to visually detect their chloride migration profile. After just a few hours, it was possible to observe the penetration depth of chloride in the specimens. Afterwards the average and maximum chloride penetration depth were measured and the chloride migration coefficient was calculated.

3.4. Carbonation depth

The carbonation test was performed on treated and untreated core samples in a climatic box, with a controlled atmosphere (CO_2 concentration 20 ± 2%, temperature 25 ± 5 °C and relative humidity 70 ± 5%). The treated and untreated faces of the samples were kept free, to allow the best exposure to the CO_2 circulating in the chamber. After 25 and 60 d in the climatic box, the cores were broken longitudinally and an alcoholic solution of phenolphthalein was immediately sprayed on the inner surfaces, for the colorimetric evaluation of the carbonation depth (UNI EN 13295).

3.5. Microstructure characterization

Environmental Scanning Electron Microscopy, ESEM, in combination with Energy Dispersive X-ray Spectroscopy, EDS (Philips ESEM-FEG XL30, operating at 10 kV in the high vacuum mode using a back scattering detector) was performed on the $20 \times 20 \times 20$ mm^3 cubes of the concrete with w/c 0.45, treated with ethyl silicate (see Section 2.4).

After curing, the treated cubes were first cut in two halves, dried at 110 °C for 48 h and finally stored in a desiccator for thermal equilibration. The specimens were then impregnated under vacuum with a low viscosity epoxy resin, polished and coated with a thin carbon film in order to improve the conductivity and prevent

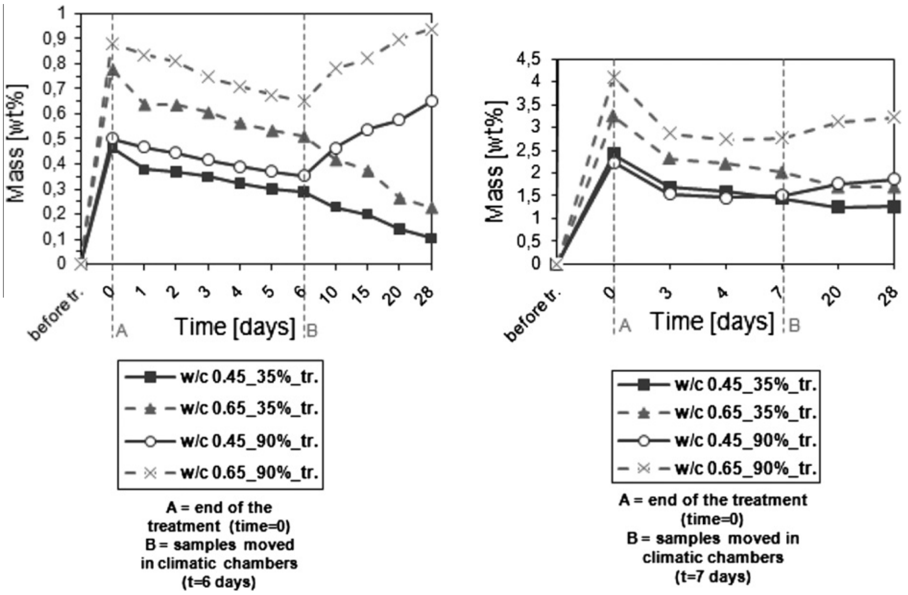

Fig. 1. Mass variation of the w/c 0.45 and w/c 0.65 (left) slabs, (right) cubic specimens.

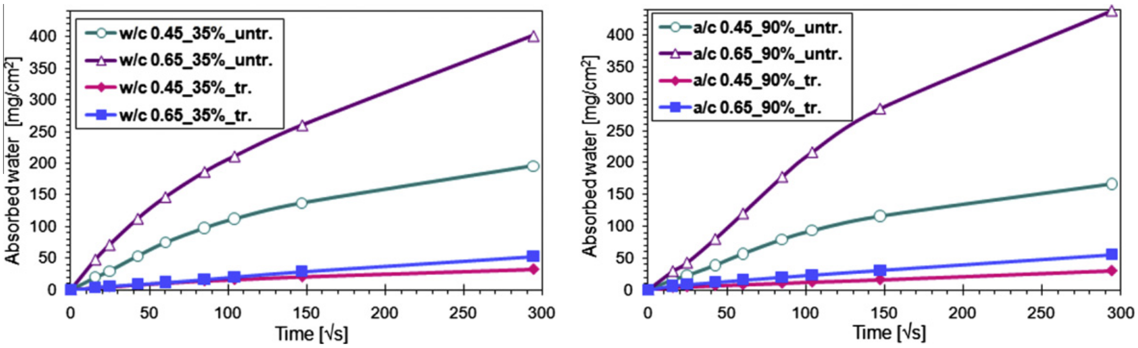

Fig. 2. Water sorptivity test on the w/c 0.45_35%, w/c 0.65_35% cores (left) and on the w/c 0.45_90%, w/c 0.65_90% ones (right) (average of three measures).

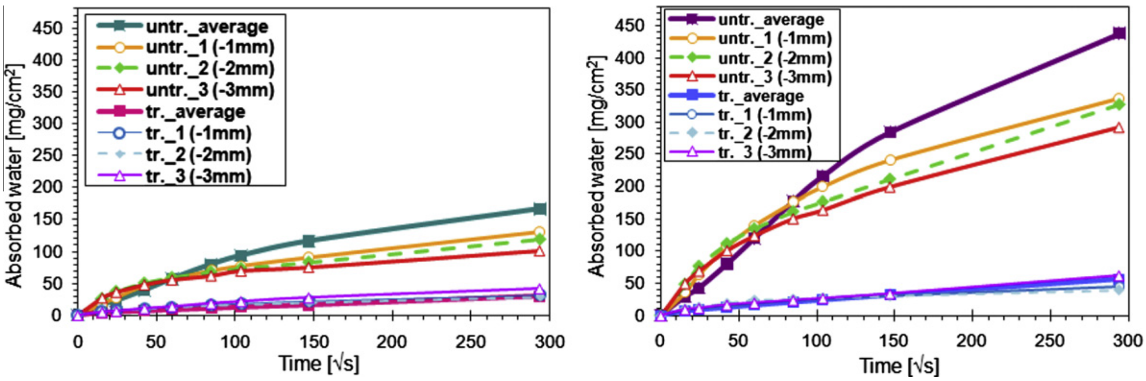

Fig. 3. Water sorptivity test on the w/c 0.45_90% (left) and the w/c 0.65_90% (right) sliced cores.

surface charging. The investigation was performed on an area close to the surface, at depth $\leqslant$1 mm.

3.6. Colour change of the treated surfaces

Quantitative analysis of the surface colour was performed on concrete samples by an Eye-One Spectrophotometer equipped with Profile Maker software. Spectra were recorded from 380 to 730 nm, and $L^*a^*b^*$ colour parameters were measured for 25 patches on each surface. Measurements were carried out on both untreated and treated slabs at the beginning and at the end of curing. The generated $L^*a^*b^*$ file allows the determination of a colour vector representing each analyzed surface. $L^*a^*b^*$ is, indeed, a perceptibly uniform 3D colour space, where colour vectors can be rep-

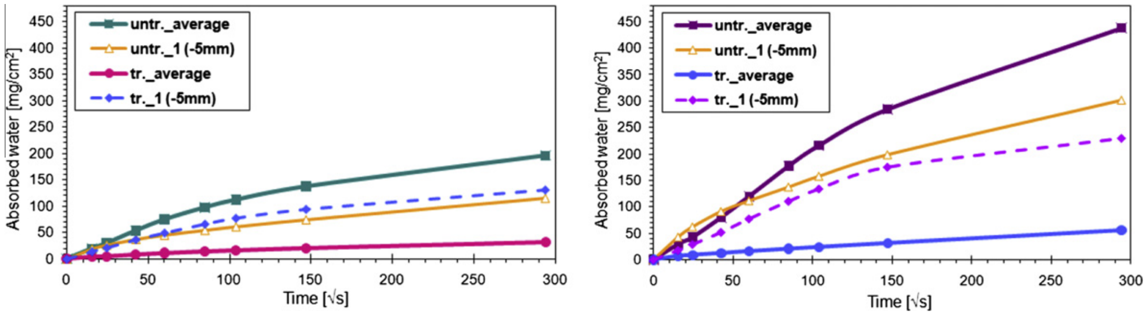

Fig. 4. Water sorptivity test on the w/c 0.45_35% (left) and the w/c 0.65_35% (right) sliced cores.

Table 4
Mean results from the chloride resistance test on the w/c 0.45_35% and w/c 0.65_35% samples.

		w/c 0.45_35%	w/c 0.45_35%	w/c 0.65_35%	w/c 0.65_35%
		untr.	tr.	untr.	tr.
Average chloride penetration depth	mm	11.6	0.25	41.2	0.75
Maximum chloride penetration depth	mm	15.0	1.0	47.5	1.5
Chloride migration coefficient	10^{-12} m²/s	7.6	0.1	20.4	0.3

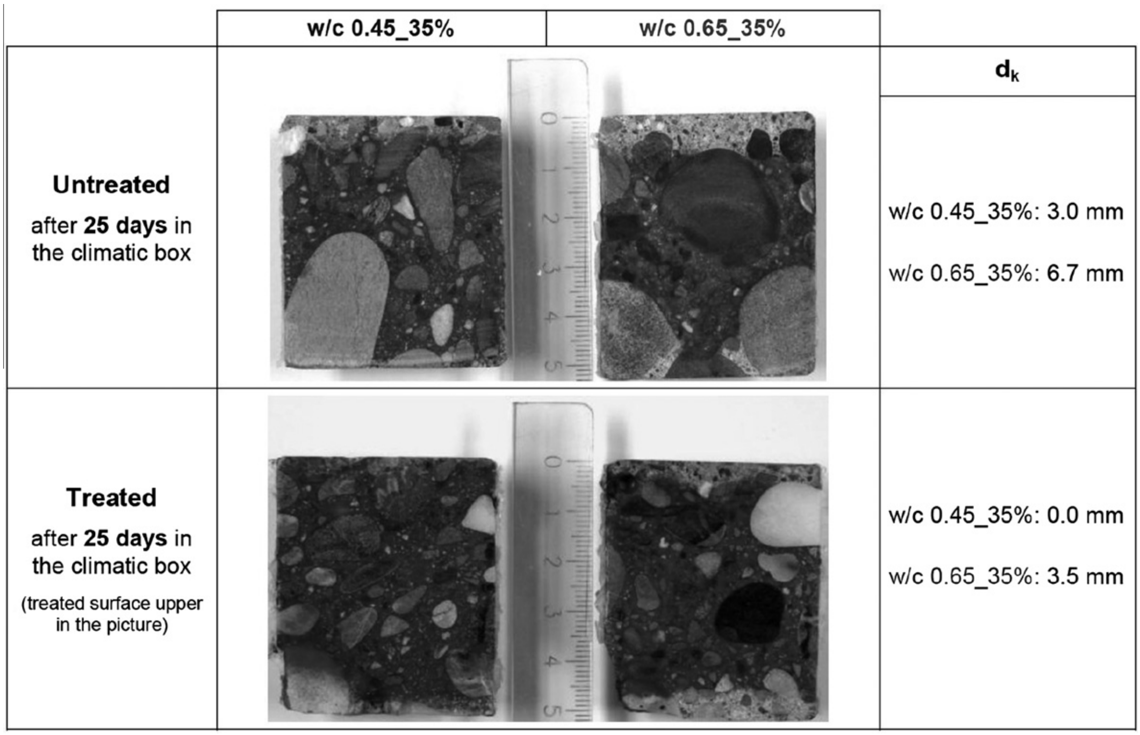

Fig. 5. Results of the carbonation depth in w/c 0.45 and in w/c 0.65 samples after 25 d in the carbonation chamber (d_k = mean carbonation depth).

resented and determined by the coordinates *a* and *b*, while *L* represents the brightness. The CIE 1976 $L^*a^*b^*$ colour parameters were calculated and, by comparing the untreated and treated samples, the colour changes were expressed as length difference vectors, obtained by $[(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{0.5}$.

The relevant spectrum file was used to plot graphs with spectral values (*y*-axis) depending on the light wavelength (*x*-axis), in the range 380–730 nm. The comparison between the untreated and treated samples was performed by evaluating the shift among the curves, which is correlated to the change in brightness, and the change in the curve shape, representing the colour variation.

4. Results

4.1. Mass variation during treatment and curing

The mass of the 150 × 150 × 50 mm³ concrete slabs (treated by brushing on one face) and the 20 × 20 × 20 mm³ cubes (treated by immersion) was measured before and after the treatment and the relevant results, in terms of mean ethyl silicate consumption per unit area, are reported in Table 3.

The mass variation of the specimens during their 28 d curing is reported in Fig. 1, respectively on the left for the slabs

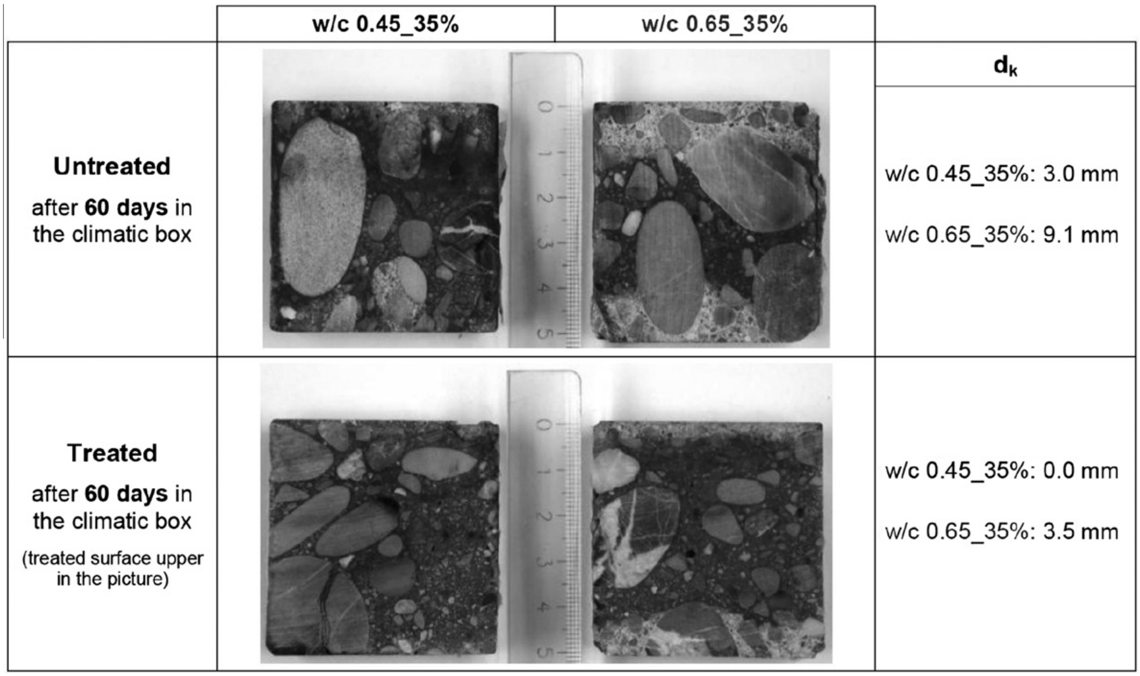

Fig. 6. Results of the carbonation depth in w/c 0.45 and in w/c 0.65 samples after 60 d in the carbonation chamber (d_k = mean carbonation depth).

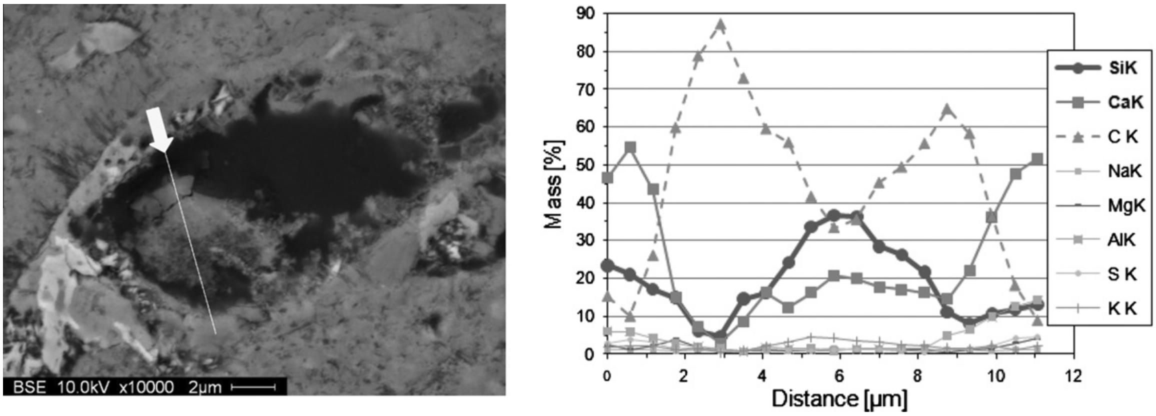

Fig. 7. Sample w/c 0.45_90%: pore partially filled with calcium silica gel, due to the reaction between penetrated ethyl silicate and portlandite (left). The chemical profile (right) was analyzed along the white line in the left picture.

($150 \times 150 \times 50\ \text{mm}^3$) and on the right for the cubes ($20 \times 20 \times 20\ \text{mm}^3$).

4.2. Water sorptivity

Fig. 2 shows the results of the water sorptivity test for the w/c 0.45_35%, w/c 0.65_35%, w/c 0.45_90% and w/c 0.65_90% cores.

The results of the sorptivity test on the sliced cores (−1 mm, −2 mm, −3 mm, −5 mm respectively) are reported in Figs. 3 and 4.

4.3. Chloride resistance

From the results obtained by the colorimetric tests, average and maximum chloride penetration depth and chloride migration coefficient were determined (Table 4).

4.4. Carbonation depth

The results of the colorimetric test performed on the concrete samples after 25 and 60 d of accelerated carbonation are reported in Figs. 5 and 6 (d_k = mean carbonation depth).

4.5. Microstructure characterization

In Fig. 7 (left) an example ESEM image of the sample w/c 0.45_90% shows a pore partially filled with a compound deriving from the consolidation treatment can be observed. The EDS linear

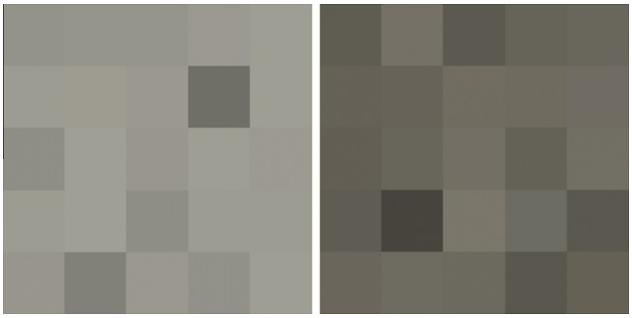

Fig. 8. Lab matrices of w/c 0.45 untreated (left) and treated (right) samples, at the beginning of the curing.

Fig. 9. Lab matrices of w/c 0.45 untreated (left) and treated (right) samples, at the end of the curing.

analysis performed on such a compound gave the composition profile in Fig. 7 (right). The detected carbon (C) is present in the pores impregnated with epoxy.

4.6. Colour change of treated surfaces

Examples of the $L^*a^*b^*$ matrices of the samples are given in Figs. 8 and 9, respectively at the beginning and at the end of the curing. In Table 5, the relevant length of the difference vectors, calculated from the average of $L^*a^*b^*$ values are reported. Figs. 10 and 11 show the spectrum plots at the beginning and at the end of the curing, respectively, for the two concretes.

5. Discussion

5.1. Mass variation during treatment and curing

As reported in Table 3, the consumption of ethyl silicate (g/cm^2) was higher for the w/c 0.65 samples than for the w/c 0.45 ones, obviously due to the different microstructure, i.e. the larger open porosity connected to the higher w/c ratio. Moreover, the consumption of ethyl silicate (g/cm^2) was higher when applied by brushing as opposed to dipping. As a matter of fact, during the treatment by brushing, some solvent has time to evaporate between the product applications, hence leaving some volume free for subsequent product absorption. On the contrary, the penetration of ethyl silicate during the 24-h immersion is limited to the amount absorbed by capillarity and no further absorption is made possible by solvent evaporation.

In Fig. 1, the decrease in the samples mass after the treatment is due to the solvent and ethanol evaporation; after moving the samples to the climatic chambers, the mass increased for the samples at RH 90%, while it continued to decrease for the samples at RH 35%.

Table 5
Length of difference vectors, calculated from the average of $L^*a^*b^*$ values, between treated and untreated samples, at the beginning and at the end of the curing.

	w/c 0.45	w/c 0.65
At the beginning of the curing	18.1	16.2
At the end of the curing	5.7	2.6

5.2. Water sorptivity

The results in Figs. 2–4 show that the treatment with ethyl silicate greatly limits the concrete's water sorptivity, with a considerable advantage in terms of expected concrete durability. The reduction rate of the water sorptivity was higher for the w/c 0.65 samples than for the w/c 0.45 ones, as a result of the higher ethyl silicate absorption (Table 3) and of the ensuing reduction of the porosity. However, the two different hygrometric conditions of curing did not significantly influence the results obtained by the water sorptivity test.

A penetration depth of ethyl silicate equal to 3–5 mm was assessed in both types of concrete, by means of repeated water sorptivity tests on concrete cores from which a layer of increasing thickness was removed starting from the impregnated surface. As a matter of fact, when 1–3 mm were removed away, the water sorptivity profiles of treated and untreated samples remained very different from those of the untreated ones (Fig. 3). After 5 mm were removed, they became substantially identical (Fig. 4).

In Figs. 3 and 4, the water sorptivity profiles of the sliced untreated samples are lower than the ones of the original cores, probably as a consequence of the cut. In fact, proceeding from the surface toward the inner of the cores the amount of cement matrix decreased and progressively more aggregates were sectioned. For the treated samples it was the opposite: the water sorptivity profiles of the sliced cores are higher than the ones of the original cores, because of the decreasing silica gel amount from the surface inwards.

5.3. Chloride resistance

The application of ethyl silicate provided a substantial reduction of the chloride penetration for both kinds of concrete. This result is well represented in Table 4. Chloride penetration was nearly absent in the treated samples; on the other hand, in the untreated ones the penetration was easily visible as a brighter area in the cement matrix. In the untreated w/c 0.65 cores, as well as in the treated ones (even if less visible), the chloride penetration depth was

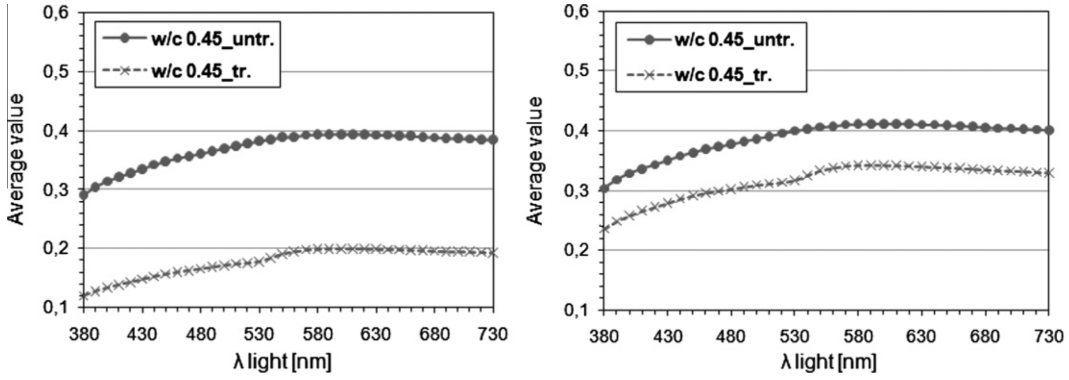

Fig. 10. Spectrum plots of w/c 0.45_35% untreated and treated samples, at the beginning (left) and at the end (right) of the curing.

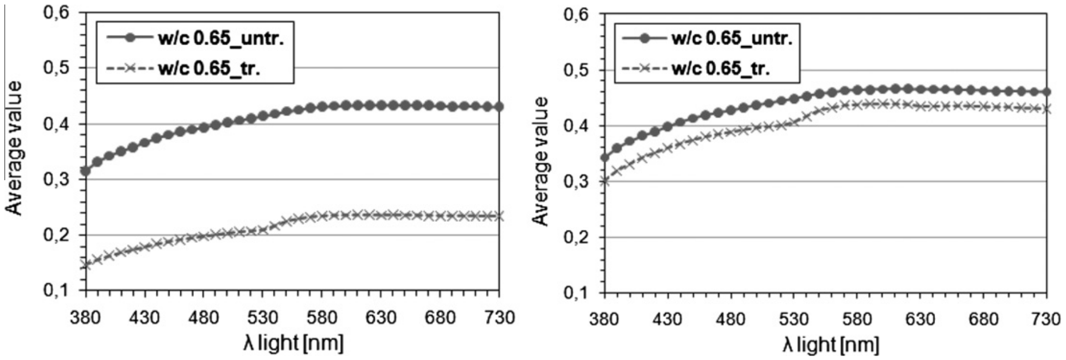

Fig. 11. Spectrum plots of w/c 0.65_35% untreated and treated samples, at the beginning (left) and at the end (right) of the curing.

higher than in the corresponding cores of concrete w/c 0.45, as expected due to their larger porosity. In conclusion, the comparison between the untreated samples and the treated ones showed that ethyl silicate is a very efficient barrier against penetration and migration of chlorides into the tested materials.

5.4. Carbonation depth

The results obtained from the colorimetric test (Figs. 5 and 6) demonstrated that ethyl silicate greatly limited the penetration of CO_2 in both types of concrete, the carbonation depth being 0.0 and 3.5 mm for the treated w/c 0.45 and 0.65 samples, respectively. Moreover, while the carbonation depth of the untreated samples increased during the carbonation test (e.g. the w/c 0.65 untreated samples passed from 6.7 to 9.1 mm after 25 and 60 d respectively), the carbonation depth of the treated samples remained the same.

The effect of ethyl silicate as a barrier toward CO_2 penetration was noticeable in both concretes. However in concrete w/c 0.45, the gas penetration was significantly lower than in concrete w/c 0.65, as a consequence of its more compact microstructure.

5.5. Microstructure characterization

From the ESEM–EDS analysis, it was possible to identify the presence of silica gel deposited mainly in the finest pores (as evidenced also in the TEOS treatment of other kind of porous materials [18]). The silica gel contained some calcium indicating a chemical interaction between the penetrated ethyl silicate and portlandite (of the cement matrix/Fig. 7). This aspect confirms the pozzolanic behaviour of the ethyl silicate in presence of free calcium hydroxide, explained in detail in the first part of the paper [15]. In [15] mixtures of TEOS and hydrated lime were prepared and the reaction between ethyl silicate and calcium hydroxide, forming calcium silicate hydrate (CSH), was shown.

5.6. Colour change of treated surfaces

For both concrete types, soon after the treatment, the treated surfaces were substantially darker than the untreated ones. However, after 4 weeks of curing, differences in colour were less noticeable, as confirmed by the values of the length difference vectors in Table 5 and by the spectrum plots, reported in Figs. 10 and 11.

For both concretes the most relevant changes were in brightness and not in colour. During the curing, the length of the colour difference vector (Table 5) decreased, indicating a reduction in colour changes. The final colour difference vector lengths ($\leqslant 5$) [18] showed very negligible colour alterations of the surfaces.

The spectrum data showed an overall shift among the curves of untreated and treated samples (Figs. 10 and 11) at the beginning of curing, due to a darker colour of the treated surfaces, and similar curve shapes, representing the colour. At the end of curing, the shift among the curves was reduced, as confirmed by the $L^*a^*b^*$ results (Figs. 8 and 9 and Table 5).

6. Conclusions

Ethyl silicate, applied by brushing onto the surface of concrete with different w/c (0.45 and 0.65), was able to penetrate up to a depth of about 3–5 mm into the concrete and induced a substantial decrease in water sorptivity, despite the low quantity of product absorbed. At the same time, reductions of chloride migration depth and carbonation depth were detected on the same samples.

Microstructural investigation showed a selective distribution of ethyl silicate within the concrete: the reaction products were apparently mainly deposited in small pores, due to capillary suction. Evidence of chemical interaction with the substrate and calcium silica gel formation was found.

Finally, the colour change of the treated surfaces was also measured, to assess the suitability of the ethyl-silicate treatment for architectural concrete. The impact of the treatment was minimal, showing very low brightness and colour changes soon after the treatment, which further decreased in time.

In summary, surface treatment of concrete with ethyl silicate appears to be a viable impregnation technique in order to increase the durability of new and existing concrete structures.

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