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Ethyl silicate for surface protection of concrete: Performance in comparison with other inorganic surface treatments

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ABSTRACT

The protection of concrete surface from environmental aggressions is often a basic issue for the enhancement of its durability. Due to the unsatisfactory long-term performance of many organic products and the subsequent need for frequent re-application, growing interest has been recently addressed toward inorganic materials. In the present study, ethyl silicate, widely used for the consolidation of weathered stones in architectural restoration and recently investigated for surface treatment of reinforced concrete structures, is compared with some inorganic products based on sodium silicate and nanosilica, generally used for the protection of concrete floors. Performance and effectiveness of the treatments are investigated in terms of morphology and microstructure; water absorption rate; water contact angle; chloride, carbonation and abrasion resistances. The results obtained highlight ethyl silicate, among the products investigated, as the most effective protection treatment for reinforced concrete structural elements.

1. Introduction

Concrete is one of the most widespread materials in modern and contemporary constructions. As a consequence of the exposure to aggressive environment, concrete structures may be affected by many chemical and physical–mechanical degradation processes, such as sulfate attack, reinforcement corrosion due to chloride penetration, carbonation and freezing–thawing [1].

In the recent decades, the deterioration of reinforced concrete structures has become a major concern and the necessity and, sometimes, urgency of intervention is evident to ensure the structures preservation. For this purpose, considerable resources are commonly used to repair and rehabilitate degraded structures, and the cost of repair is sometimes even higher than the original investment [2]. Therefore, preventive and protective measures are recommended [2] to avoid a premature deterioration of new concrete structures (especially in highly aggressive environments) and to increase the durability of old ones.

Many protective materials and methods for reinforced concrete are currently available [3]; among these, surface treatments are widely used to improve the resistance of such concrete cover against the penetration of aggressive substances, both in new and existing structures, in order to prevent the durability loss of new concrete structures, or to extend the service life of the existing ones [4].

The surface protection treatments for concrete are classified into three groups by EN 1504-2:2004 [5]: *hydrophobic impregnation* (producing a water-repellent surface, with no pores filling effect), *impregnation* (reducing the surface porosity, with partial or total pores filling effect) and *coatings* (producing a continuous protective film on the concrete surface). Hydrophobic impregnation [6,4] is usually performed through silane- or siloxane-based water repellent products, that penetrate into concrete pores and, theoretically, react with hydrated cement particles, forming a reaction product that acts a hydrophobic lining on the pore walls [4]. Organic polymers are currently used for impregnation and coating in order to create a physical barrier that prevent the environmental aggressive agents from penetrating into concrete [6].

However, such organic products exhibit several drawbacks, such as quick loss of their initial properties due to outdoor exposure (UV, oxygen, temperature, humidity, pollutants, etc. [6]), and more in general a limited durability, as well as poor physical–mechanical compatibility with concrete, possibly leading to cracking and detachment [7,8]. As an alternative to organic treatments, the use of inorganic products for concrete surface protection has been proposed. These products are mainly aqueous solutions of sodium silicate, also known as “waterglass”, and, to a much smaller extent, potassium silicates and fluosilicates [6,9]. Sodium and potassium silicates were first tried as stone consolidants in 1855 [10]. In concrete, soluble sodium silicate is expected to react with portlandite in the cement matrix, forming calcium-silicate hydrates and sodium hydroxide. As a result, an improvement in concrete properties, such as a lower permeability, a greater hardness and an overall durability enhancement [9], is

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expected. So far, experimental evidences of the performance of sodium silicate for concrete protection are limited [4], and the mechanism and effects in reducing the water and chloride penetration and in improving the carbonation resistance are still not fully clarified. Moreover, the possible increase in the risk of alkali–silica reaction, due to the formation of sodium hydroxide, should be taken into account [6].

The performance of products based on nanoparticles in dispersion have been recently discussed too [11,12], and aqueous dispersions of nanosilica, with or without the addition of sodium silicate have been recently commercially proposed for surface treatment of concrete floors. As described for the "waterglass" treatment, their performance and efficacy for the protection of the surface are still scarcely investigated in literature.

Encouraging results for the protection of concrete surface have been recently obtained with ethyl silicate treatment [6]. Ethyl silicate (also known as TEOS, i.e. tetraethylorthosilicate) is mainly known as a consolidating material for weathered stones in architectural restoration [13]. This alkoxysilane compound is usually applied onto the surface in solution with low viscosity organic solvents. Once penetrated into the pores, it undergoes a two-stage curing process leading to the precipitation of amorphous silica gel inside the stone pores [14]. The reasons for the wide use of ethyl silicate for stone consolidation (especially the silica-rich ones) are mainly its small monomer size and low viscosity, leading to deep penetration into the substrate, and its volatile and not damaging by-products released during hardening (ethanol and water). Moreover, the final reaction product (silica gel) exhibits a good compatibility with stone and a good durability, unlike many polymeric consolidants [6,15]. In a previous study [6], ethyl silicate showed good performance when applied on concrete surface: thanks to its good impregnation ability (3–5 mm penetration depth) and to its pozzolanic behavior with portlandite [16], it induced a dramatic decrease in capillary suction, chloride diffusion coefficient and carbonation depth.

In this paper, the effectiveness of ethyl silicate, sodium silicate solutions and aqueous nanosilica dispersions (with or without sodium silicate addition) for surface treatments of reinforced concrete structures are investigated and compared, in terms of morphology and microstructure; water absorption rate; water contact angle; chloride, carbonation and abrasion resistances.

2. Materials

2.1. Concrete samples

Two concrete mixtures based on blast furnace slag cement, CEM III/A 42.5R ("concrete 1") and calcareous cement, CEM II/B-LL 32.5R ("concrete 2"), both with water to cement ratio (w/c) 0.65, cement amount 300 kg/m^3, total aggregate amount 1824 kg/m^3 (maximum size 15 mm), acrylic superplasticizer (Dynamon SR41, Mapei, 0.65 wt% respect to cement) were prepared. The two types of cement were selected in order to consider both an ordinary concrete ("concrete 2") and a concrete with improved durability ("concrete 1"). The high w/c ratio (0.65) was chosen in order to simulate the scarce properties and performance of deteriorated and/or low quality concretes. Concrete cubes of size $10 \times 10 \times 10$ cm^3 were manufactured and cured for 24 h (h) at $T = 20$ °C and 95 ± 3% relative humidity (RH), then demoulded and immersed in water for 14 days (d) and, after a high-pressure washing, kept in a climatic chamber at $T = 20 \pm 1$ °C and RH = 50 ± 5% for further 13 days, in order to ensure constant moisture content throughout the samples at the end of the 28-days curing. The conditioning at $T = 20 \pm 1$ °C and RH = 50 ± 5% (also recommended as pre-conditioning before the water absorption test, according to UNI 7699) was selected as representative of typical thermo-hygrometric conditions experienced by concrete in the field; moreover, these are the climatic conditions usually recommended by manufacturers of the protective treatments for the application procedures.

At 28-days, the mean compressive strength (average of two samples) of concretes 1 and 2 amounted to 44.8 ± 1.1 N/mm^2 and 31.5 ± 0.9 N/mm^2 respectively.

2.2. Protective treatments

For the protection of concrete surface, an alcoholic ethyl silicate solution (**ES**) was prepared by mixing 75 wt% of TEOS and 25 wt% of ethanol.

For comparison sake, the following inorganic protective treatments were considered: an aqueous sodium silicate solution, **SS**; an aqueous dispersion of nanosilica (particles diameter about 100 nm), **NS** diluted with water (ratio 1:4) just before the application and an aqueous dispersion of nanosilica with a small addition of sodium silicate, **NS-SS**. Table 1 shows the main chemical–physical characteristics of the materials used.

Once cured, some concrete specimens were treated on all the faces (by dipping for 24 h) and on one face only (by brushing wet on wet), in view of the tests to be performed. The features and the application recommendations of the different treatments were considered. The same method and procedure (brushing application repeated six times in a day for 3 subsequent days) for all the products were chosen, for better comparing their effects. A repeated application of the products was considered suitable for the treatment of reinforced concrete structures (not involving areas as wide as floors); moreover, this somehow meets the recommendation of several manufacturers of consolidating/protecting materials (e.g. application 'until rejection' for ES, 15-min-long spraying for NS).

The specimens are indicated with the prefix **1**- and **2**-, corresponding to the concretes 1 and 2 respectively, and the abbreviation of the materials used for the protective treatment (ES, SS, NS, NS-SS). Untreated samples are indicated as **UNTR**.

2.3. Curing after treatment

At the end of the treatment, the specimens treated with ethyl silicate were left under a ventilated hood ($T = 25 \pm 1$ °C; RH = 50 ± 5%) for about 1 week, in order to enhance the first and more substantial evaporation of the solvent. Then the samples were cured for about 1 week in a climatic chamber at $T = 20 \pm 1$ °C, RH = 45 ± 1% and, for further 2 weeks, at room conditions ($T = 21 \pm 1$ °C, RH = 50 ± 5%). For the other three treatments, the specimens were directly cured at room conditions for the whole 4 weeks. These curing conditions

Table 1
Main chemical–physical characteristics of the products used.

Product	Dry weight content (2 h, 120 °C) (wt%)	pH	Density (at 25 °C) (g/cm^3)	ICP-AES analysis (%)				FT-IR
				SiO$_2$	Na$_2$O	K$_2$O	SO$_3$	
SS	20.0	11.1	1.19	10.90	3.81	0.01	0.00	Alkaline silicate
NS	15.4	10.8	1.11	11.79	1.08	0.00	0.02	Silica
NS-SS	6.7	11.3	1.13	3.82	1.14	0.03	0.00	Alkaline silicate, silica
ES	40.0	–	0.89	21.38	–	–	–	Ethyl silicate in ethanol

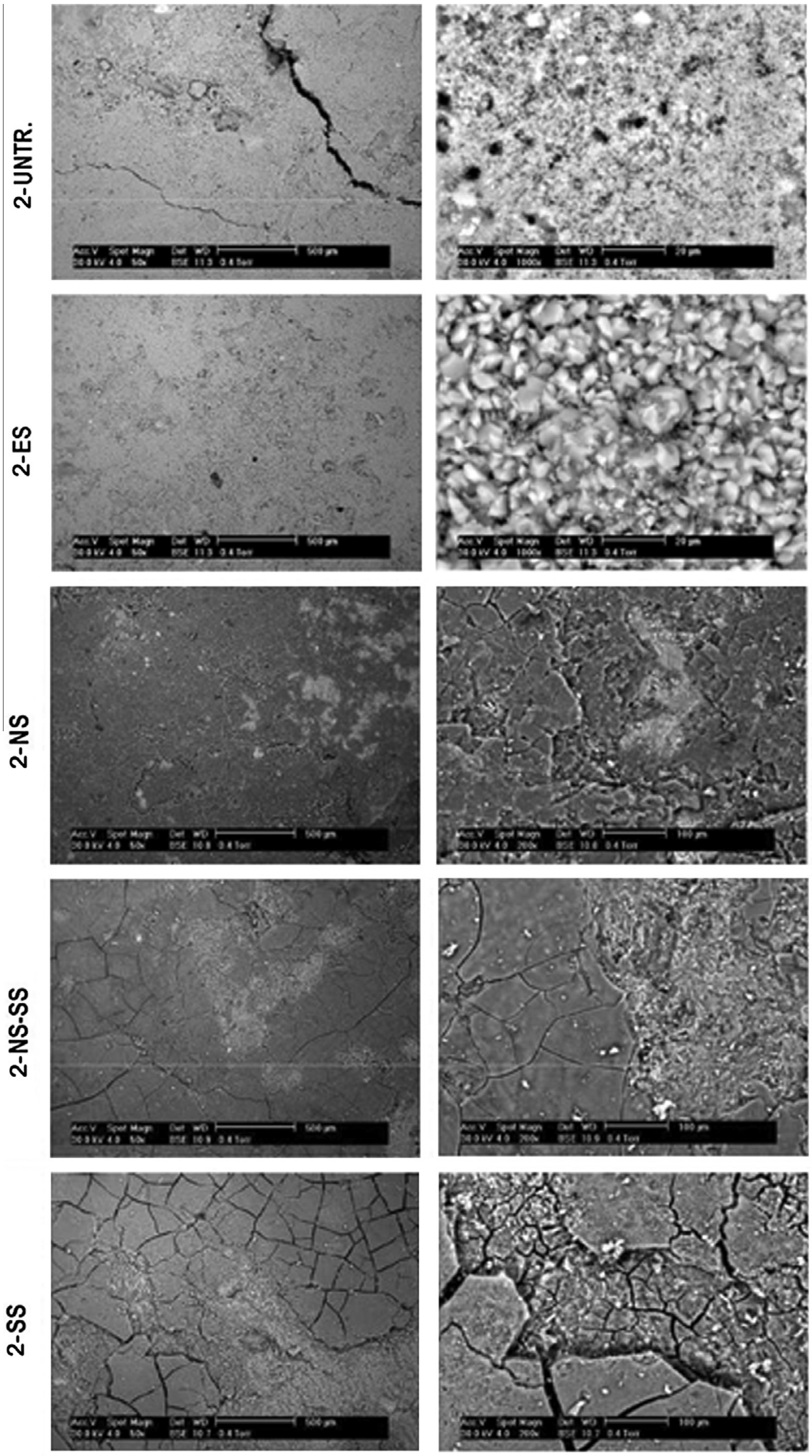

Fig. 1. ESEM images of untreated and treated samples of concrete 2 (external surface analysis).

were chosen to ensure a good outcome of the treatments, according to the technical recommendations provided by the relevant manufacturers.

3. Methods

3.1. Product consumption determination

In order to determine the product consumption, the samples were weighed before and immediately after the treatment, with an accuracy of 0.01 g. Although a certain weight loss is expected to occur due to solvents evaporation, the weigh gives an approximate idea of the quantity of protective material absorbed by the concrete samples.

3.2. Morphology and microstructure characterization

Environmental Scanning Electron Microscopy, ESEM, in combination with Energy Dispersive X-ray Spectroscopy, EDS (Philips ESEM-FEG XL30, operating at 30 kV in the low vacuum mode using a back scattering detector) were performed on external surfaces and cross sections (depth 1 mm from the external surface) of concrete treated on one face and of untreated concrete. The specimens were cut from the cubes and dried at 110 °C for 48 h. The samples for the analysis of cross section were then impregnated under vacuum with a low viscosity epoxy resin and polished before the observation.

The ESEM–EDS analysis was performed only on concrete 2, as concrete 1, due to its higher quality, was significantly less improved by the tested treatments, as described in the following (Section 5).

3.3. Water absorption

As water ingress into concrete is directly or indirectly responsible for all its degradation processes, the resistance of the treated/untreated samples to water ingress was investigated.

The water absorption test was performed on the cubic samples treated on all the faces (one for each treatment) and on the untreated ones for comparison, according to UNI 7699:2005, by keeping them totally immersed in water. Samples were weighed

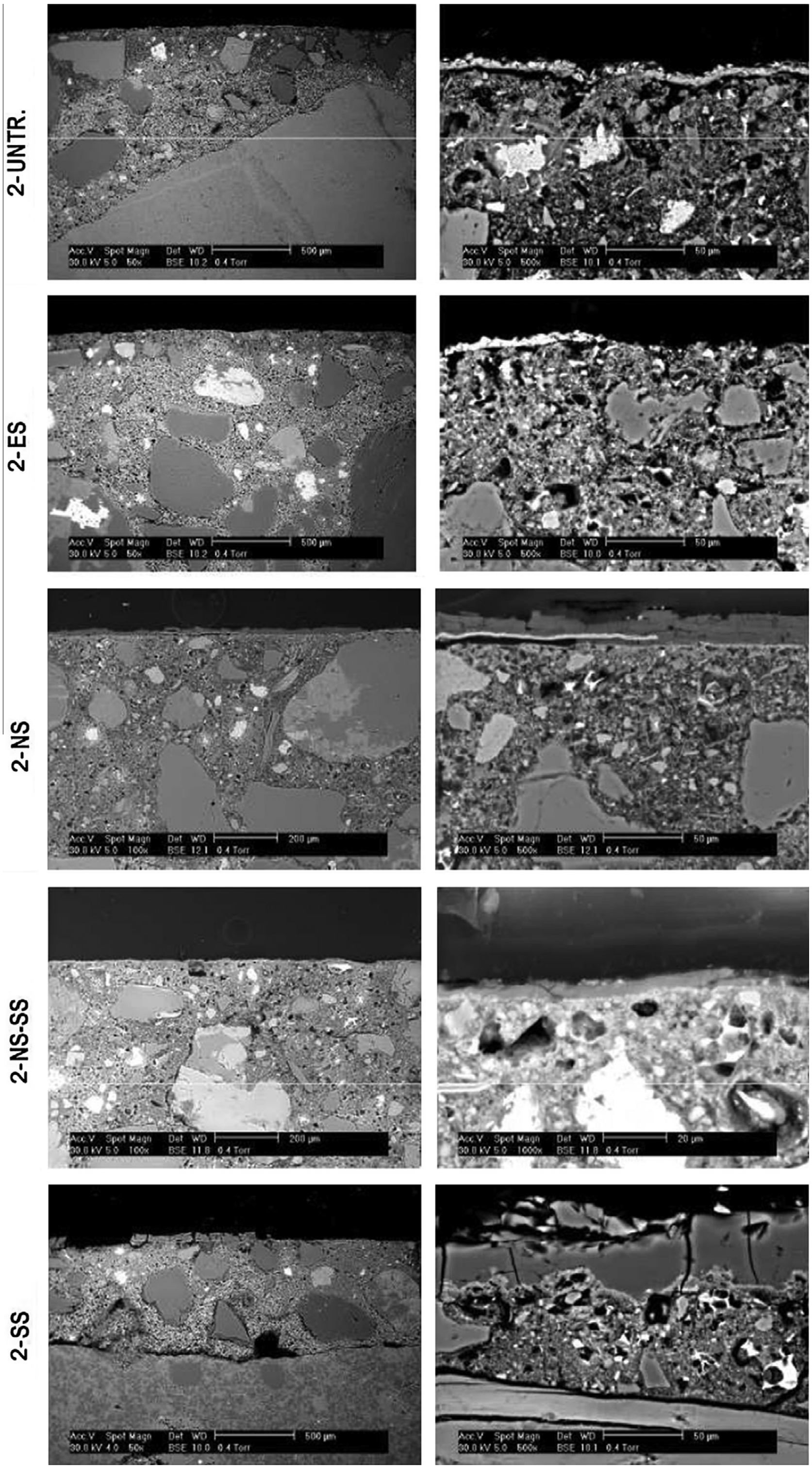

Fig. 2. ESEM images of untreated and treated samples of concrete 2 (cross section analysis).

in surface-dry conditions after 1, 3, 6, 24 h and 2, 3, 4, 7 days and the water absorption percentage after 7 days ($WA_{7\ days}$) was determined.

The water permeability coefficient after 24 h of water sorptivity test ($w_{24\ h}$) and the relevant classification according to UNI EN 1062-3:2001 were also evaluated.

3.4. Water contact angle and absorption time

In order to evaluate the surface hydrophobic effect of the treatments, the water contact angle was measured on four different points of specimens treated on one face and of untreated ones by a DSA 10 Krüss Instrument. A water drop of known volume was released on the concrete external surface by a flat needle placed from a known distance, determining the contact angle and the time required for the complete water drop absorption.

3.5. Chloride resistance

The performance of the treatments in limiting the migration of chloride within concrete was evaluated by the chloride resistance test. Cubic samples treated on all the faces (one for each treatment) and untreated were immersed in deionized water until saturation (for about 1 week). Then the specimens were kept immersed in a 10% NaCl aqueous solution. After 7 and 40 days of permanence in the NaCl solution, the cubes were broken and fluorescein and silver nitrate solution 0.1 N were sprayed on the freshly broken surfaces (Swiss standard SIA 262/1) [17]. The samples were then dried in an oven at 50 °C for 24 h in order to enhance the visual detection of their chloride migration profile.

3.6. Carbonation resistance

In order to investigate the effectiveness of the treatments in increasing the carbonation resistance of concrete, cubic samples treated on all the faces (one for each treatment) and untreated were placed in a climatic box, with CO_2 concentration 20 ± 2%, $T = 25 \pm 5$ °C and RH = 70 ± 5%. After 5, 12, 25 and 60 days of permanence in the climatic box, a slice of about 1–2 cm was cut from each cubes and an alcoholic solution of phenolphthalein was immediately sprayed on the inner surface, for the colorimetric evaluation of the carbonation depth according to UNI EN 13295:2005.

3.7. Abrasion resistance

Resistance to abrasion is an important parameter for the assessment of surface treatment performance. An abrasion test was performed on samples treated on one face (one for each treatment) and on untreated ones, according to UNI EN ISO 5470:2001. For a correct placement of the sample on the Taber Model 503 Standard Abrasion Tester, a 5 mm hole was made in the center of each sample. Taber abrading wheels H22 (type: non-resilient; composition: vitrified; abrasive action: very coarse) and two 500 g steel calibration weights were used for the test. A speed of 60 rpm was used. The weight loss profile and the final weight loss after 300 revolutions were evaluated. The color difference between the abraded and not abraded area was visually observed as well.

4. Results

4.1. Product consumption determination

The product consumption referred to the different treatments was 0.41, 0.29, 0.16 and 0.22 g/cm^2 for ES, NS, SS, NS-SS respectively.

4.2. Morphology and microstructure characterization

ESEM images of external surfaces and cross sections of the concrete 2 samples can be observed in Figs. 1 and 2 respectively. The slightly darker zone in the cross section of the untreated concrete sample (Fig. 2) may be ascribed to traces of the epoxy resin penetrated during vacuum impregnation before the ESEM observation (Section 3.2).

4.3. Water absorption

Fig. 3 shows the results of the water absorption test for the concretes 1 (on the left) and 2 (on the right).

The water permeability coefficient after 24 h ($w_{24\ h}$), the relevant classification according to UNI EN 1062-3:2001 and the water absorption percentage after 7 days ($WA_{7\ days}$) according to the definitions in UNI 7699:2005, are reported in Table 2.

4.4. Water contact angle and absorption time

The results of the water contact angle and of the water drop absorption time measurements are reported in Table 3. As the results were quite scattered (depending on the point of measurement) for all the investigated samples, the results in Table 3 were averaged on four points.

4.5. Chloride resistance

The results of the colorimetric test performed on the concrete samples after 7 (on the left) and 40 (on the right) days of immersion in a 10% NaCl solution are reported in Fig. 4 (d_m = mean chloride migration depth). The chloride migration profile can be recognized as a brighter area in the concrete.

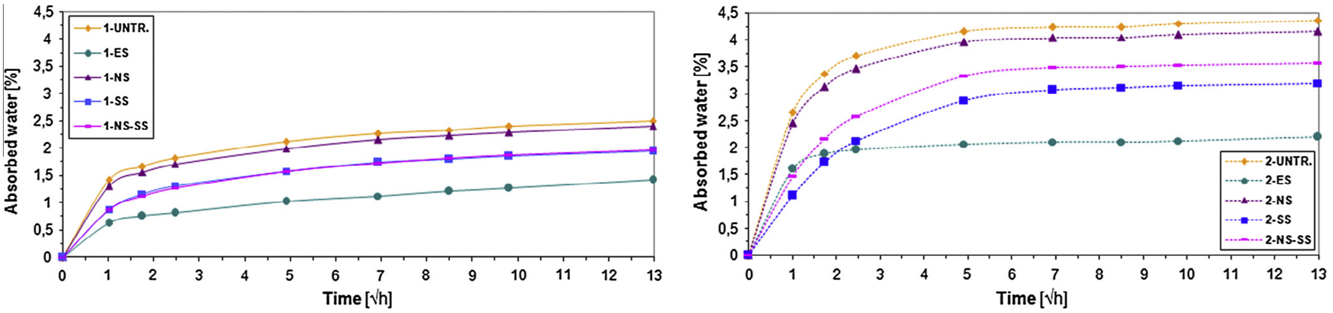

Fig. 3. Water absorption test according to UNI 7699:2005 on untreated and treated samples of concretes 1 (left) and 2 (right).

Table 2
Water permeability coefficient ($w_{24\,h}$) with the relevant classification and water absorption percentage ($WA_{7\,days}$) of untreated and treated samples.

Sample	$w_{24\,h}$ (kg/(m^2 $\sqrt{h}$))	Classification of the $w_{24\,h}$ according to UNI EN 1062-3:2001	$WA_{7\,days}$ (%)
1-UNTR.	0.184	Medium class	2.49
1-ES	0.081	Low class	1.42
1-NS	0.192	Medium class	2.40
1-SS	0.170	Medium class	1.94
1-NS-SS	0.167	Medium class	1.98
2-UNTR.	0.356	Medium class	4.37
2-ES	0.116	Medium class	2.20
2-NS	0.459	Medium class	4.15
2-SS	0.349	Medium class	3.20
2-NS-SS	0.311	Medium class	3.56

Table 3
Contact angle and absorption time of a drop of water on the external surface of concrete samples (average of four measures).

Sample	Contact angle (°)	Time for the water drop absorption (s)
1-UNTR.	36 (±1)	6
1-ES	48 (±1)	25
1-NS	24 (±2)	7
1-SS	25 (±2)	16
1-NS-SS	24 (±1)	29
2-UNTR.	32 (±3)	5
2-ES	62 (±1)	10
2-NS	27 (±3)	21
2-SS	19 (±4)	12
2-NS-SS	40 (±9)	16

4.6. Carbonation resistance

The results of the colorimetric test performed on the concrete samples after 5 (on the left) and 60 (on the right) days of accelerated carbonation are reported in Fig. 5 (d_k = mean carbonation depth).

4.7. Abrasion resistance

Table 4 and Fig. 6 show the results of the Taber abrasion test. The weight loss is reported in Table 4, while Fig. 6 depicts the weight loss profile of the concretes 1 (on the left) and 2 (on the right) as a function of the number of revolutions.

5. Discussion

The consumption of ES (0.41 g/cm^2) was higher with respect to the other products (0.16–0.29 g/cm^2), probably due to the different solvents used (ethanol in ES and water in NS, SS and NS-SS). In fact, compared to water, ethanol is characterized by a lower surface tension and contact angle, and so a higher wetting ability.

The ESEM–EDS analysis of the external surface and cross-section of untreated concrete 2 (Figs. 1 and 2) showed the presence of three main zones: (i) the crust laitance (a weak and non-durable layer consisting of cement, fine aggregates and impurities, brought to the surface by the bleeding water [18]); (ii) zones where the detachment of the crust laitance has occurred and the underlying concrete surface is observable; (iii) occasional cracks, probably due to shrinkage.

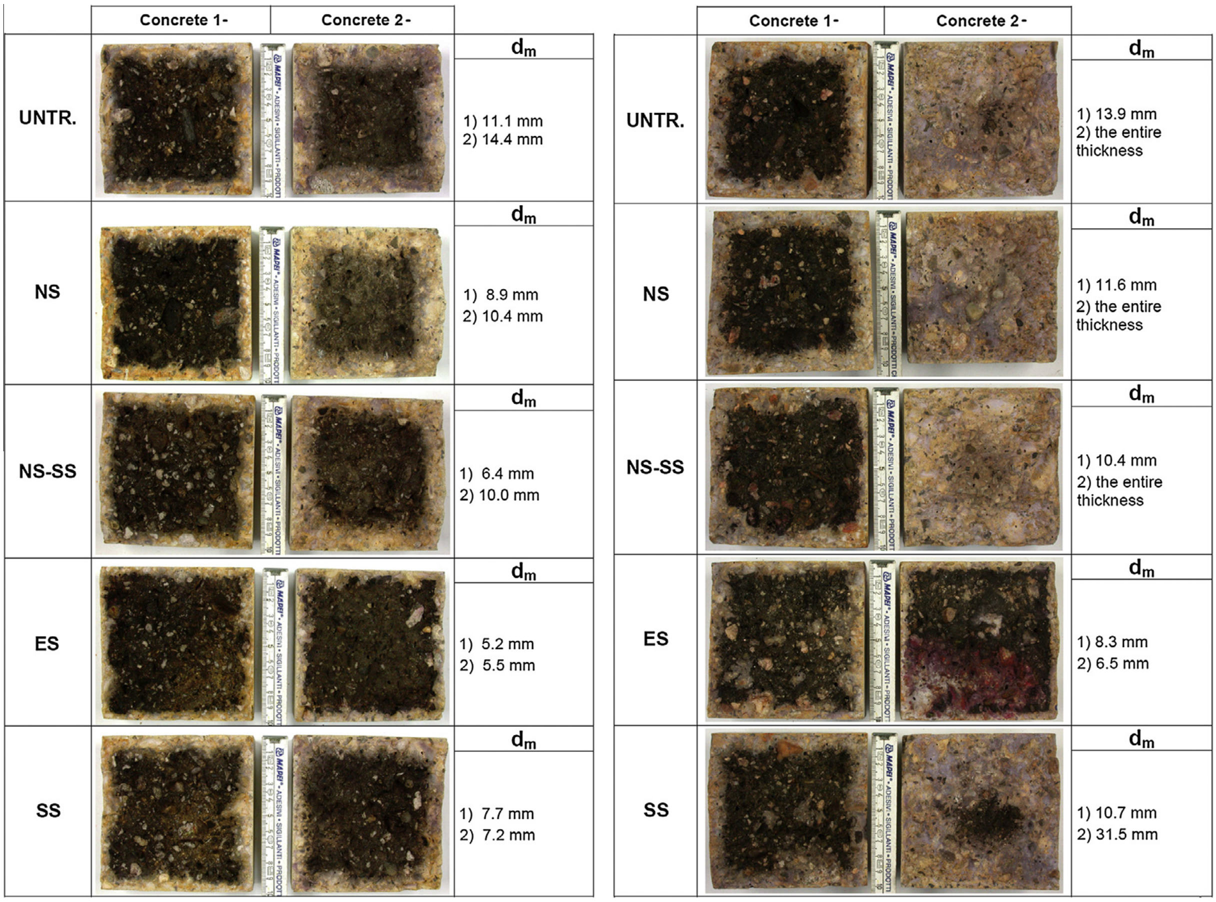

Fig. 4. Results from the chloride resistance test on the concretes (1 and 2) samples, after 7 days (left) and 40 days (right) of immersion in a 10% NaCl solution (d_m = mean chloride migration depth).

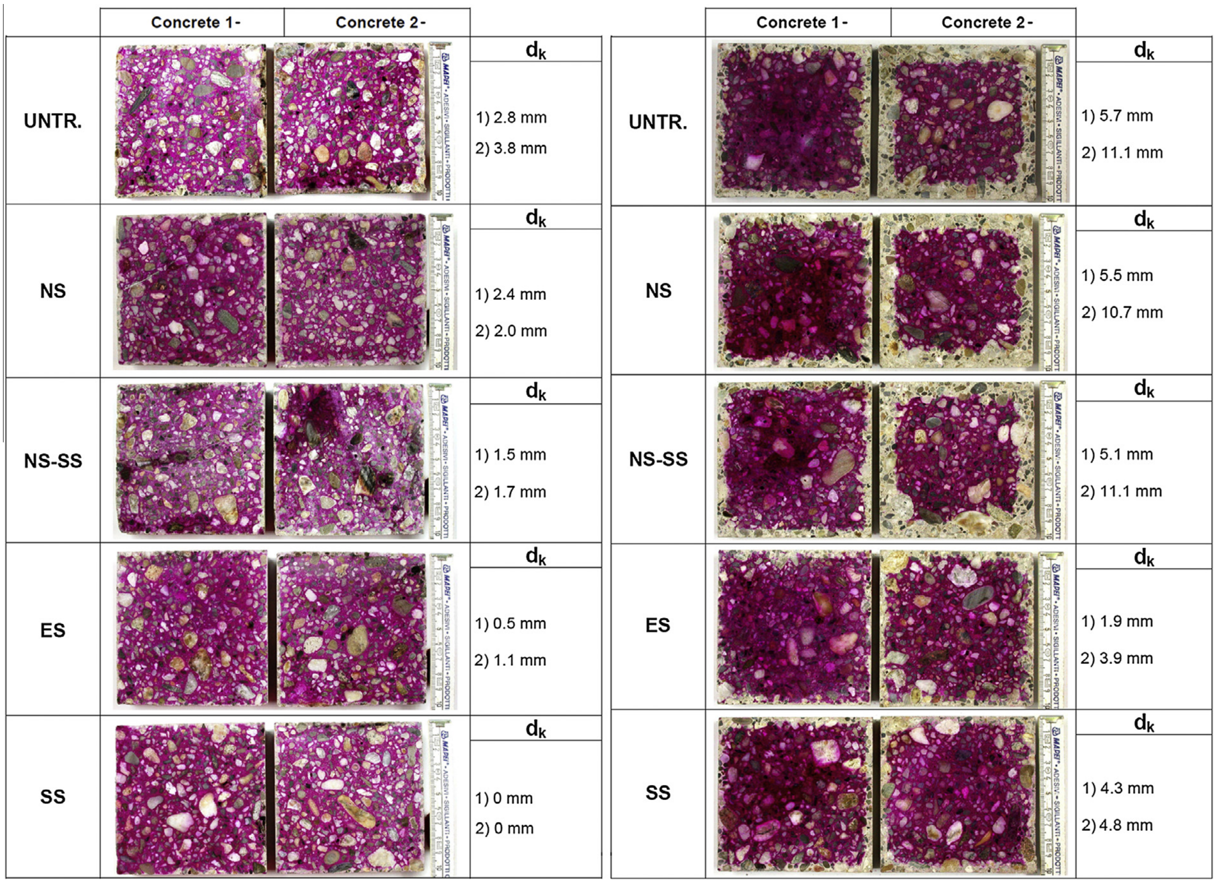

Fig. 5. Carbonation depth in concretes (1 and 2) samples after 5 days (left) and 60 days (right) in the carbonation chamber (d_k = mean carbonation depth).

Table 4
Weight loss due to the abrasion test performed on concrete samples.

Sample	Weight loss (mg)
1-UNTR.	2440
1-ES	1230
1-NS	1910
1-SS	820
1-NS-SS	1020
2-UNTR.	2770
2-ES	1900
2-NS	2590
2-SS	1440
2-NS-SS	1980

Concrete treated with ethyl silicate (2-ES in Figs. 1 and 2) exhibits a more compact and less detached crust laitance if compared to the untreated concrete, due to the presence of silica gel, performing a consolidating effect (EDS confirmed the increase in the silicon amount in this zone). Under the surface (Fig. 2), the microstructure appears a bit more compact, but with no pore occlusion effect. It was not possible to detect the exact distribution of silica gel in the pores, firstly due to high SiO_2 content of the original material (making the detection of silica by EDS more difficult) and secondly due to the pozzolanic reaction probably occurred between silica gel and portlandite [16], giving C–S–H barely distinguishable from the hardened cement paste. Conversely, the other products (NS, NS-SS and SS) were deposited in multiple layers on the concrete surface (Figs. 1 and 2); in some cases, the layers are locally cracked and/or detached. Where the layer is detached, either the crust laitance or the underlying concrete surface are visible. The only ES treatment did not produce any film-forming effect.

The water absorption of the untreated samples (Fig. 3 and Table 2) is much lower in concrete 1 than in concrete 2, as expected due to the different kind of cement used (blast furnace slag cement and calcareous cement, respectively), despite the same w/c ratio and cement amount. All the treatments lead to a decrease in the water absorption: such decrease is minimum for NS and significant for the other ones. ES provides the best performance in limiting the water ingress into concrete, with a significant improvement in terms of expected durability: in both concretes 1 and 2 the water absorption after 7 days is approximately one half with respect to the untreated samples.

In terms of contact angle and water absorption time (Table 3), the treatment with ES was the only one that provided an increment of both of them, in concretes 1 and 2. The hydrophobic effect of ethyl silicate for stone consolidation was pointed out also in literature, but contrasting opinions were reported about its duration (6 months or more) [10,15]. The treatment with nanosilica (NS), sodium silicate (SS) and nanosilica with sodium silicate (NS-SS) led to a decrease in the contact angle, probably due to the hydrophilic nature of the deposited material [19]. However, the presence of a compact (although cracked) layer on the surface also reduces the time for water absorption, consistently with the reduction of water absorption in Fig. 3.

The chloride penetration was of course higher in concrete 2 than in concrete 1, as expected due to the different porosity of the two concretes, owing to the different cement used. Such chloride penetration was not limited by nanosilica (NS) and nanosilica with sodium silicate (NS-SS) treatments: no differences in the chloride migration profile can be noticed for any kinds of concrete and any time of immersion in NaCl solution (Fig. 4). On the contrary, the application of ES provides a substantial reduction of

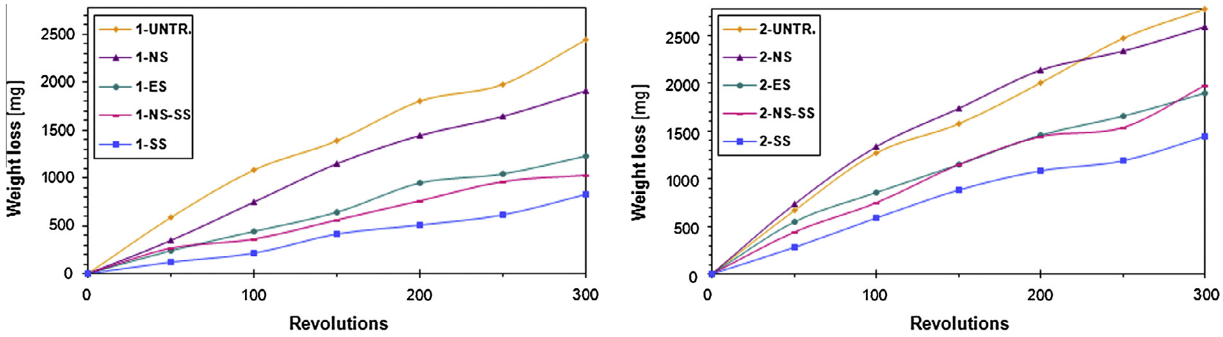

Fig. 6. Abrasion test on untreated and treated samples of concretes 1 and 2.

the chloride penetration for both concretes 1 and 2, at 7 days and at 40 days. Treatment with sodium silicate (SS) showed an only slight reduction of the chloride penetration depth after the first 7 days of immersion in the NaCl solution. The poor protective effect of NS, NS-SS and SS in limiting the chloride ingress seems due to the cracking and detachment tendencies of the deposited layers, as shown by ESEM images (Figs. 1 and 2).

The results of the accelerated carbonation test (Fig. 5) show that only two treatments limit the penetration of CO_2 in both the types of concrete: ES and SS. Among them, ES exhibited the best performance for long time of exposure in the carbonation chamber (60 days): the carbonation depth varied from 5.7 to 1.9 mm in concrete 1 and from 11.1 to 3.9 mm in concrete 2. The other two products (NS and NS-SS) did not provide any reduction in the carbonation depth, as probably the film deposited on the surface was thinner and more brittle than the SS one, and hence, more prone to detachment.

In Fig. 6 and in Table 4 the results of the abrasion test are compared. The treatment with sodium silicate (SS) provided the best performance in increasing the surface abrasion resistance of both concretes, again owing to the remarkable thickness of the external layer formed: the weight loss reduction respect to the untreated sample was about 66% for concrete 1 and 48% for the concrete 2, while it was only 58% and 29% for concretes 1 and 2 respectively treated with NS-SS and 50% and 31% for those treated with ES. Conversely, NS treatment was ineffective, especially for concrete 2, probably owing to the scarce thickness and consistency of the layer formed from the silica nanoparticles.

6. Conclusions

The results so far obtained point ethyl silicate as a promising surface treatment for reinforced concrete protection. Three other inorganic treatments, generally proposed as surface treatment of concrete floors, were tested in comparison with ethyl silicate: an aqueous sodium silicate solution, an aqueous dispersion of nanosilica and an aqueous dispersion of nanosilica with a small addition of sodium silicate. While ethyl silicate penetrates into concrete and reduces, once hardened, its permeability without any pore occlusion or film forming effect, the other products give multiple surface layers, locally cracked and detached.

Ethyl silicate provided the best performance in limiting the water ingress into both concrete types, while the other products were not so effective (or even completely ineffective). In terms of chloride and carbonation resistance, only the application of ethyl silicate and sodium silicate produced a significant improvement and, and in particular, the treatment with ethyl silicate gave the best performance for both short and long time of exposure to chloride and carbon dioxide.

The results described, together with a good resistance to abrasion, highlight that ethyl silicate is the most successful protection treatment for reinforced concrete structural elements, among the products investigated in this study.

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