SURFACE TREATMENT OF CONCRETE WITH TETRAETHYL ORTHOSILICATE, Na_2SiO_3 AND SILANE: COMPARISON OF THEIR EFFECTS ON DURABILITY

ZHAOHENG GUO*, **, #PENGKUN HOU*, **, SHIFENG HUANG*, **, NING XIE*, **, XIN CHENG*, **,
L.P. SINGH***, STROKOVA VALERIYA****, NELYUBOVA VIKTORIYA****

*Shandong Provincial Key Laboratory of Preparation and Measurement of Building Materials,
University of Jinan, Jinan, Shandong, 250022, China
**School of Materials Science & Engineering, University of Jinan, Jinan, Shandong, 250022, China
***CSIR – Central Building Research Institute, Roorkee 247 667, India
****Department of Material Science and Materials Technology, Belgorod State Technological University
named after V.G. Shoukhov, Belgorod, 308012, Russia

#E-mail: pkhou@163.com

The surface treatment of existing concrete structures with silica-based organic and inorganic agents is often used to improve the durability of the structures, but their effects vary from each other, thus the recognition of their strengths and drawbacks could help to make good use of the techniques under various environments. In this work, tetraethyl orthosilicate (TEOS), an organic precursor for manufacturing silica sol, together with other two normally used silica-based agents, Na_2SiO_3 and silane, was used for the surface treatment of concrete. Their effects on the durability were studied and compared by investigating the compressive strength, the water absorption rate, the carbonation, the chloride penetration and the sulfate attack of cement concrete samples. The results showed that TEOS decreased the transport properties of concrete significantly: reductions of 49.0 % of the water absorption rate, 28.5 % of the chloride ion penetration depth, and 20 % of the carbonisation degree to that of the control sample were found, while the corresponding values of 42 %/80 %, 39 %/71 %, and 23 %/10 % of Na_2SiO_3/ silane-treated samples were shown. The compressive strength and visual observation showed that the samples treated by TEOS exhibited the best performance for long term exposure in the 5 wt. % sodium sulfate solution when compared with silane-treated and Na_2SiO_3-treated samples. The variation of the in-situ $Ca(OH)_2$ consuming capability of the agents, as well as their effects on the hydration and hardening properties of the cement-based material could be ascribed to their differences in improving the durability.

INTRODUCTION

Cement-based materials are the most widely used building materials and cannot be fully replaced by other materials in the foreseeable period. The problems associated with the manufacturing and use of cement/ concrete is also very serious. Large amount of resources and energy are consumed, a large amount of greenhouse gas (CO_2) and pollutants (SO_x and NO_x) are produced, all of which greatly and negatively affect the natural and social environments [1]. One of the possible methods of reducing these impacts is to improve the service life of concrete structures, and a good durability of cement concrete is strongly desired [2-3].

Concrete often deteriorates under harsh environments from the surface to the inside part by means of the ingression of liquid and gaseous phases, such as water, aggressive ions, like SO_4^{2-}/Cl^-, and CO_2 migration [4-6]. Thus, the quality of the surface concrete is a governing factor that dictates the durability of the concrete structure. It is a commonly used technique of applying surface treatment to improve the surface quality [7]. Although surface treatment can hardly be good for the visible defects of concrete, its beneficial effects on the micro-defects, such as microcracks induced by shrinkage [8-10], drying and wetting [11], etc., which potentially decrease the permeability of concrete [12-14], leading to a foreseeable increase of the macro-properties of the concrete [15-16]. Generally speaking, the surface treat-ment agents can be usually grouped into two major types: (1) Organic agents, such as silane/siloxane, which help to reduce the transport of aggressive media in concrete, i.e., pores, water-proofing [17-18]. (2) Inorganic agents, such as alkali silicate, fill pores and make the surface microstructure compact [19]. Water-proofing agents applied to the concrete surface greatly reduce the mig-ration of water and change migration by absorption [20-22], but their weathering resistivity has always been ques-tioned [22-23]. On the other hand, the inorganic alkali silicate will increase the alkali ions that negatively influence the property of concrete [24].

Recently, tetraethyl orthosilicate (TEOS, $Si(OC_2H_5)_4$), a precursor of manufactured silica sol, and a rock consolidator used in art work preservation, has been used for the surface treatment of cement-based materials due to its low viscosity, deep penetration capability, and its volatile and innocent by-product (ethanol) released during its *in-situ* hydrolysis into SiO_2 [25], Equation 1. Due to the filling effect of the SiO_2 cluster formed *in-situ*, and the pozzolanic reactivity, additional C-S-H gels can form on the surface of the concrete, thus a compacter surface microstructure can be expected [26], Equation 2. The conversion of the organic silicate treatment agent into inorganic SiO_2 could avoid the disadvantages of traditional organic and inorganic agents as mentioned above.

$$TEOS + 2H_2O \rightarrow SiO_2 + 4C_2H_5OH \qquad (1)$$

$$SiO_2 + Ca(OH)_2 + H_2O \rightarrow C–S–H \text{ gel} \qquad (2)$$
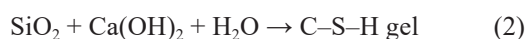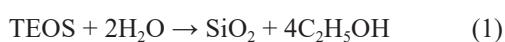
Some studies suggested that TEOS was beneficial for improving the surface quality of a cement paste/mortar [7, 25, 27-28], but it is rare to find a study on the durability of cement-based materials, especially concrete. Since concrete is normally the final product and it is greatly different from a cement paste or mortar, the recognition of the strengths and weakness of TEOS and other normal treatment agents is important when choosing a surface treatment technique for concrete structures, as the improper selection of the treatment agent contributes to the negligible improvement of the durability or even introduces negative side effects to the material [24, 29-31]. In this work, the influences of TEOS, sodium silicate and silane for the surface treatment of a cement concrete/paste are studied and compared in terms of compressive strength; water absorption rate; chloride, carbonation and sulfate attack resistance, with the hope of differentiating their effects and optimising the treatment techniques in different deteriorative environments.

EXPERIMENTAL

Materials

Ordinary Portland cement (OPC) (Chinese standard GB 175-2007 [32]) was used and its properties are listed in Table 1. A commercial tetraethyl orthosilicate (TEOS, $Si(OC_2H_5)_4$), poly-methyltriethoxysilane (silane) and sodium silicate nonahydrate (solid content of 40 wt. %) were also used in this work and their properties are listed in Table 2.

Table 2. The physicochemical properties of the treatment agents.

Product	Chemical formula	Content (wt. %)	Density (at 25°C) (g·cm⁻³)
TEOS	$(C_2H_5O)_4Si$	28.0	0.900
Na_2SiO_3	$Na_2SiO_3·9H_2O$	22.0	0.933
Silane	$C_7H_{18}O_3Si$	45.0	0.995

Methods

Sample preparation and surface treatment method

One day and 28-day old cement/concrete samples with w/c = 0.4 were surface-treated in this work. A fine aggregate with a fineness modulus of 2.9 1 and coarse aggregate with the maximum size of 20 mm were used for preparing the concrete. During mixing, the raw materials were dry-mixed for one minute and then wet-mixed for another four minutes. After mixing, the paste was cast in 2 cm × 2 cm × 2 cm moulds, and the concrete was cast in 10 cm × 10 cm × 10 cm and Φ 10 cm × 5 cm moulds. All samples were cured for 1 day in the ambient environment (ca. 25°C/60 % relative humidity (RH)) before demoulding. Surface treatment of the sample was applied before being continually cured in a chamber (20°C/95 % RH) for 1 day and 28 days. Brushing was used three times on each sample to create a surface saturation state at a time interval of 10 min.

Compressive strength

The compressive strength (Chinese standard GB/T-50081-2002 [33]) of the concrete was tested on the samples with a size of 10 cm × 10 cm × 10 cm at 3 kN·s⁻¹. The compressive strength of the paste after the sulfate attack was tested on the samples with a size of 2 cm × 2 cm × 2 cm at a displacement control mode of 1 mm·min⁻¹. The average value of the six samples was taken as the representative value.

Water absorption rate

The concrete samples were cut into a size of 10 cm × 10 cm × 1 cm for the water absorption rate test (ASTM C1584-04 [34]). The samples were dried in a vacuum chamber at 60°C for a constant weight before the test. One 10 cm × 10 cm face of the sample was left unsealed and the other five faces were sealed with an epoxy resin. The unsealed face was immersed in water and the mass change of the sample at different times was measured by an electronic balance at the saturated-surface-dry

Table 1. The chemical composition (%) and the physical properties of the cement.

SiO_2	Al_2O_3	Fe_2O_3	SO_3	CaO	MgO	LOI	Total	Density (g·cm⁻³)	Fineness (m²·kg⁻¹)
21.1	4.7	3.5	3.3	62.9	2.8	1.1	99.4	3.1	354

condition. The water absorption rate was calculated by dividing the sample's surface area (cm^2) with the increase of the sample mass (mg) at different immersion times. The water absorption rates of three samples at a certain water-immersing time were tested and averaged as the representative value.

Sulfate attack resistance

The *in-situ* calcium hydroxide consumption of TEOS [35] will reduce the CH content of concrete at the surface [27], which might be beneficial for the sulfate attack resistance. In this study, one group of cement paste samples were cured in 5 wt. % Na_2SO_4 solution (the solution was renewed once a month) for 7, 28 and 500 days before testing the compressive strength. The average value of the three samples was taken as the representative value, and the compressive strength ratio to that of the control sample at different ages were calculated and compared.

Carbonation resistance

The samples were placed in a CO_2 chamber (CO_2 concentration 99.9 % at a pressure of 0.3 MPa, temp = = 50°C, RH = 70 %). The samples after treatment and curing were dried in a vacuum chamber at 60°C for 24 or 72 hours before the test. After carbonation, the samples were cut along the intermediate section and then an alcoholic solution of phenolphthalein was immediately sprayed onto the freshly-cut surface, and the carbonation depth of ten locations were measured once per 10 mm from the edge of the surface. The average value of all the points was taken as the representative value. The evaluation of the carbonation depth was conducted according to the Chinese standard GB/T-50082-2009 [36].

Chloride resistance

The rapid chloride migration coefficient method (RCM, Chinese standard GB/T 50082-2009 [36]) was used to study the ion permeability of the concrete before and after the surface treatment. The samples (Φ 10 cm × 5 cm) were cut along the diameter and then a silver nitrate solution (0.1 mol·l⁻¹) was sprayed on the freshly cut surface to measure the ion penetration depth. The penetration coefficient of the chloride ions was calculated using the following equation:

$$D_{rcm} = 2.872 \times 10^{-6} \times Th\,(X_d - \alpha)/t$$
$$\alpha = 3.338 \times 10^{-3} \tag{3}$$

where D_{rcm} – the penetration coefficient of the chloride ions in the concrete by RCM method ($m^2·s^{-1}$); T – the average of the initial and final temperature of the anode electrolyte (k); h – sample height (m); X_d – diffusion depth of the chloride ion (m); t – test duration (s); α –auxiliary variable.

X-ray diffraction

The influences of the different treatment agents on the mineralogy of hardened cement-based materials were studied by X-ray diffraction (XRD). A powder sample was scraped out of the surface and dried in a vacuum chamber at 50°C for 24 hours and then ground into a powder (ground by an agate mortar) smaller than 75 µm before testing. A Bruker D8 Advance, Germany, was used at the acceleration voltage, acceleration current, step size and dwelling time of 40 kV, 20 mA, 0.05°, and 1 s, respectively.

RESULTS AND DISCUSSIONS

Compressive strength

The influence of the different treatment agents on the development of the compressive strength of the concrete is shown in Figure 1. Although the penetration and influencing depth of the agents could be several millimetres [23-24], its effects on the microstructure of the concrete sample on the surface may reduce the defects that propagate under load or from the environment, leading to an increase in the strength [35, 37].
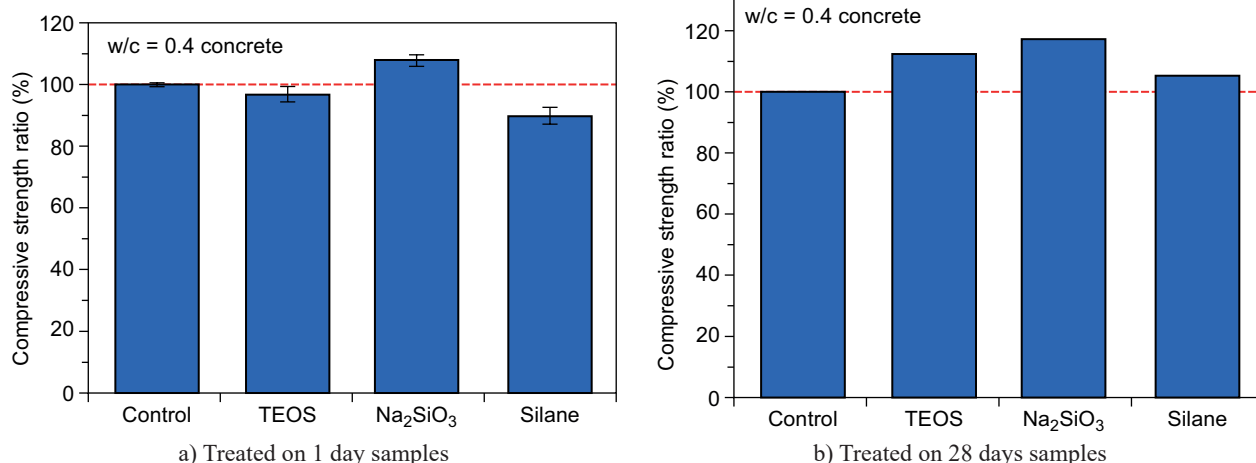

Figure 1. The compressive strength ratio of the concrete surface treated at 1 day and 28 days and then cured for 28 days (compressive strength ratio = (strength of the treated sample / strength of the control sample) × 100 %.

When the samples are treated at one day, Na$_2$SiO$_3$ increases the compressive strength when compared to the control sample. This could be due to that Na$_2$SiO$_3$ can react with the CH on the surface of concrete forming additional C-S-H and a compacter and lesser defective surface structure [38]. A slight decrease in the strength is seen in the TEOS-treated samples, and this is in line with the study that TEOS negatively affects the hydration of cement at an early age [27]. And this can also be the reason for the decrease of the compressive strength of the silane-treated concrete at the early ages [29-30].

For samples treated at 28 days, all agents increase the compressive strength of the concrete samples to various degrees, i.e., 20 % of Na$_2$SiO$_3$, 12.5 % of TEOS and 6.9 % of silane. The penetration of the agents into the concrete, and the *in-situ* hydrolysis and Na$_2$SiO$_3$ and TEOS into the silica sol, as well as the reaction of the sol with CH could be ascribed to the increase in the strength of the two agents. A higher increase of Na$_2$SiO$_3$ on the compressive strength shows its greater effect than TEOS, which could be due to their differences in penetration capability, reactivity, etc. A comparable compressive strength of the samples before and after the treatment with silane was seen and this is in consistent with other researchers [27].

Water absorption rate

The migration of water from the environment to the inner concrete often carries deteriorative ions and causes defects, and stopping water migration on the concrete surface has always been regarded as an important technique of improving the durability of concrete [30-40]. The effects of the surface-treatment of concrete samples with TEOS/Na$_2$SiO$_3$/silane on the reduction of the water absorption rate of the concrete samples are shown in Figure 2.
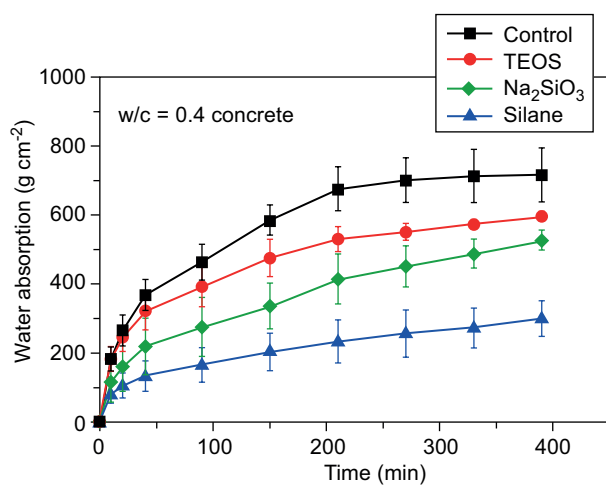
It can be seen in Figure 2 that all three agents decrease the water absorption rate on the early- and late-age treated samples to degrees of 17 %, 26 %, and 58 % (1 day) and 49 %, 42 %, and 80 % (28 days) after treatment with TEOS, Na$_2$SiO$_3$ and silane. The highest reduction of the water absorption rate is shown on the samples treated by silane, which could be due to the hydrophobicity nature of the silane-treated sample. A higher reduction rate is seen in the TEOS treated samples at the late age than that in the early age sample. The avoidance of a negative effect of TEOS on the cement hydration, as well as its *in-situ* hydrolysis and chemical reaction with Ca(OH)$_2$, contributes to this difference as shown in the compressive strength results [25, 41].

Carbonisation resistance

Carbonisation of concrete is a big concern due to the neutralisation of the reinforced concrete would lead to the protective layer fading around the reinforcement resulting in the acceleration of rusting [42]. The *in-situ* CH-consuming characteristic of the silica-based agents raises the concern of the reduction in the carbonisation resistance of concrete. Meanwhile, the compaction of the microstructure of the concrete on the surface may stop the carbonisation. The results of the colorimetric test performed on the concrete samples after accelerated carbonation are shown in Figure 3.

For samples treated at one day, the results show that all the agents reduce the carbonisation depth to degrees of 2.4 % (TEOS), 2.4 % (silane), and 23 % (Na$_2$SiO$_3$) of the w/c 0.4 concrete samples. At 28 days, TEOS reduces to about 20 % while the Na$_2$SiO$_3$-treated sample shows a comparable result with that of the control. These results indicate that TEOS is less effective than Na$_2$SiO$_3$ in carbonisation resistance when treated at 1 day, while it is much better than Na$_2$SiO$_3$ when treated at 28 days. The advantage of Na$_2$SiO$_3$ in reducing carbonisation at early age shows its positive effects in compacting

a) Treated on 1 day samples
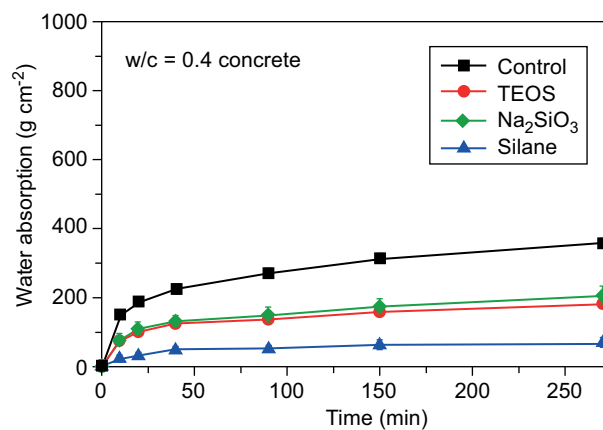
b) Treated on 28 days samples

Figure 2. The water absorption of the concrete surface-treated at 1 day and 28 days and then cured in standard conditions (20°C and 90 % RH) for 28 days.

the concrete, which could be due to both the cement hydration acceleration effect of the Na^+ and the formation of a C–S–H gel, while the negative effect of TEOS on the hydration of cement at the early age could be ascribed to the comparable carbonisation degree with that of the control, even when considering the advantages of it.
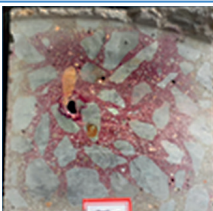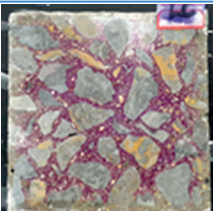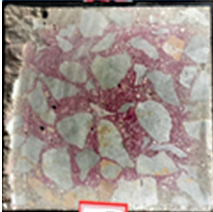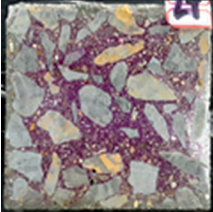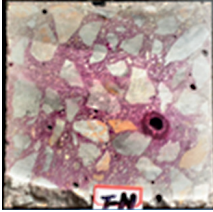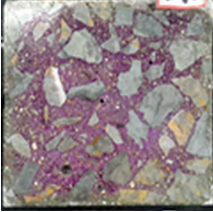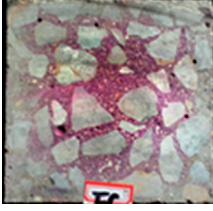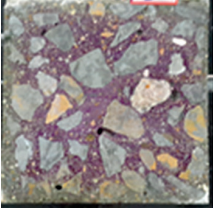
At the later treatment age, the *in-situ* formed silica sol and the newly formed C–S–H gel of TEOS physically blocks the CO_2 transportation to a potential degree although Na_2SiO_3 shows higher pozzolanic reactivity (Figure 1), and this is in line with the result shown in Figure 2. For silane, it rarely affects the carbonisation process of the concrete, and this could be accounted for its negligible effect on the physical filling effect on the concrete pores [27].

Chloride resistance

A chloride ion is a typical ion for measuring the permeability of cement-based materials [43-45]. The permeability varies according to the porosity [46-47], the composition [48], the C–S–H gel characteristic [49-50], the wettability [17], etc., of the cementitious materials. All these features will change when they have been applied with a surface treatment. The results of the penetration coefficient of the chloride ions (D_{rcm}) on the concrete samples are shown in Figure 4, which shows the comprehensive effect of the results. The chloride migration profile can be recognised as a brighter area in the concrete.

It can be seen that the reduction of the chloride penetration depth of the samples treated by TEOS, Na_2SiO_3 and silane are 28.5 %, 39 %, 71 %, respectively, when compared with the control sample at an early age. The sample treated by silane showed the best performance in decreasing the chloride penetration depth, and this could due to the hydrophobicity introduced by the silane: water as a carrier of chloride ions cannot be transported into the cement concrete, thus leading to a higher reduction of ion penetration depth. Both silicate treatment agents, TEOS and Na_2SiO_3, show a positive effect in decreasing the ion penetration at a very early age and the latter showed a better effect. These indicate that although TEOS retards the hydration in cement, resulting in a decrease of the

1 day	w/c = 0.4	Carbonation depth (mm)
Control		10.50
TEOS		10.25
Na_2SiO_3		8.00
Silan		10.25

a) Treated on 1 day samples

28 days	w/c = 0.4	Carbonation depth (mm)
Control		5.00
TEOS		4.00
Na_2SiO_3		5.00
Silan		4.50

b) Treated on 28 days samples

Figure 3. The carbonisation of the concretes samples treated at 1 and 28 days: a) carbonated for 24 hours; b) carbonated for 72 hours.

compressive strength as shown in Figure 1, its benefits for decreasing the transport property from the *in-situ* hydrolysis forming a silica cluster and its *in-situ* reaction with cement overtakes the negative influence brought on by the retardation on the cement hydration.

At a later age, for samples treated by TEOS, Na$_2$SiO$_3$ and silane, 7 %, 7 % and 14 %, respectively, reductions of the chloride penetration depth is shown when compared to the control samples. It can also be obviously seen that samples treated at 28 days show a relatively small

a) Treated on 1 day samples

b) Treated on 28 days samples
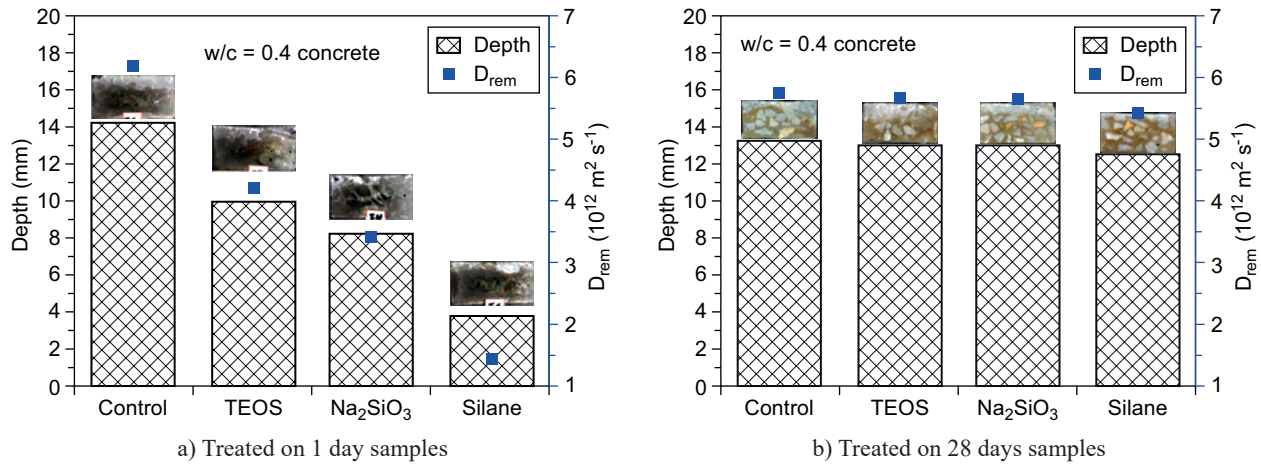
Figure 4. The chloride resistance of the concrete samples treated with different agents.

a) Treated on 1 day samples

b) Treated on 1 day samples

c) Treated on 28 days samples

b) Treated on 28 days samples

Figure 5. The compressive strength ratio of the paste samples cured in 5 % Na$_2$SO$_4$ solution. (the samples were firstly treated and then cured in standard conditions (20°C, 95 % RH) for 28 days before being moved into the Na$_2$SO$_4$ solution cured for a different duration, the compressive strength ratio = (strength of the treated sample / strength of the control sample) × 100 %

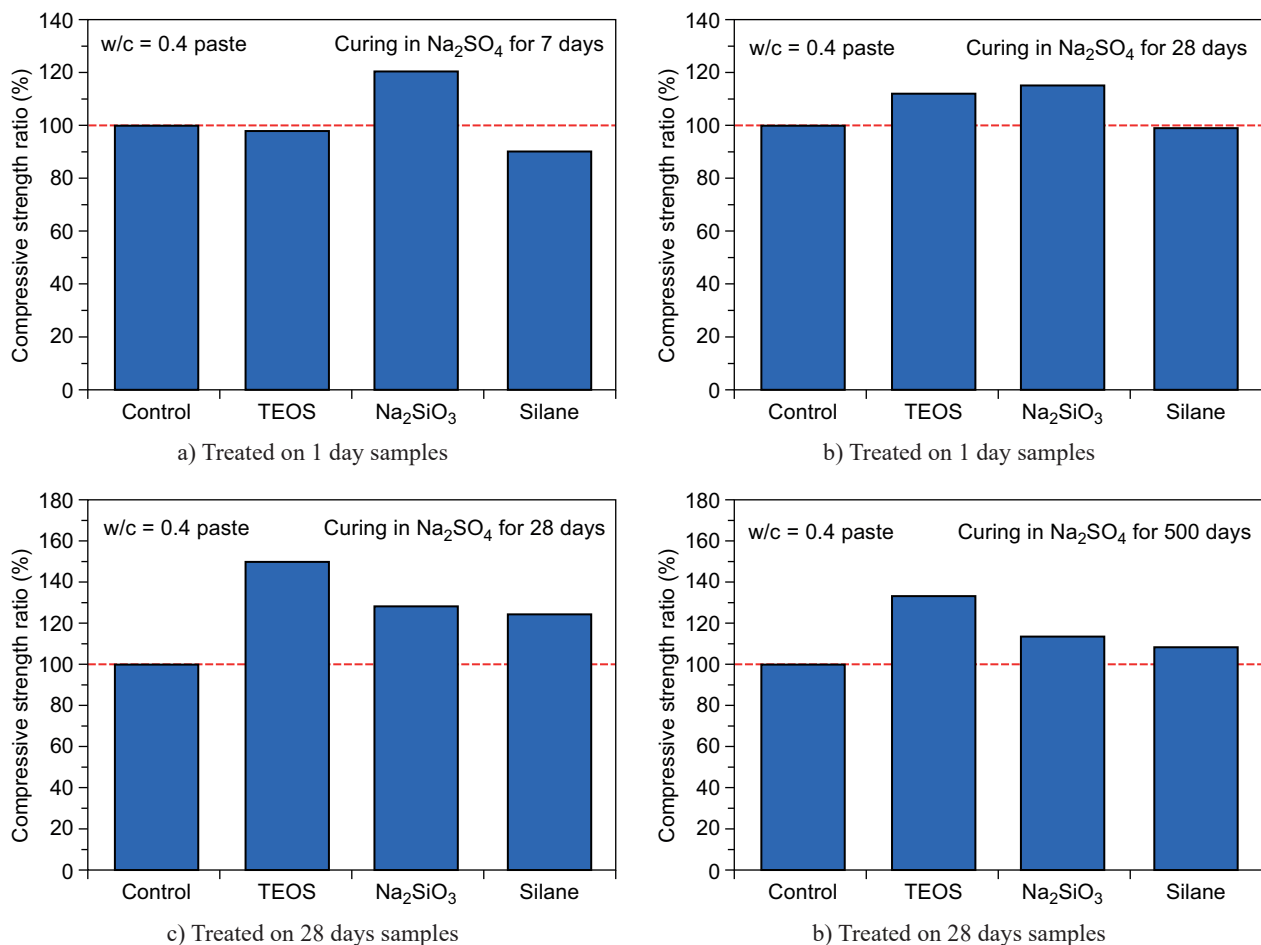improvement of the chloride ion resistivity, and a much higher ion penetration coefficient is seen in the later age treated sample. As the samples were about 1 or 2 months old when they had been surface-treated, the maturity of the samples is comparable, thus the difference is related to the alternation of the nature of the concrete surface with different agents. A relatively higher penetration depth and reaction degree of the agents treated at the very early age sample and then the standard-cured for 28 days could be the reason for TEOS and Na_2SiO_3 [25, 51-52]. For the silane-treated sample, condensation of the agent on the fresh concrete could more thoroughly happen [53], leading to a higher reduction.

Sulfate attack resistance

Due to the $Ca(OH)_2$ consuming property of the treatment agents, the sulfate attack resistivity of the treated sample may change. The compressive strength ratio of the samples before and after the treatment with the different agents was compared, and the results are shown in Figure 5.

For samples treated 1 day after casting and then cured in standard conditions for 28 days, it shows that Na_2SiO_3 has a positive effect while TEOS is comparable and silane has a negative effect on the strength when the samples were continually cured in the sodium sulfate solution for 7 days. However, when continually cured for 28 days, both the TEOS and Na_2SiO_3 treated samples are stronger than the control sample, and the comparable strength is seen with the silane-treated sample. This shows that the organic agents, i.e., TEOS and silane negatively affect the strength gain of the samples at a very early age, and this is more obvious in the 7-day cured sample. The higher strength of the Na_2SiO_3 and TEOS treated samples to that of the control sample shows the beneficial effect of these agents on the improvement of the surface quality, and the superior performance of the Na_2SiO_3 could be due to the acceleration of the cement hydration of the sodium ions at an early age [54].
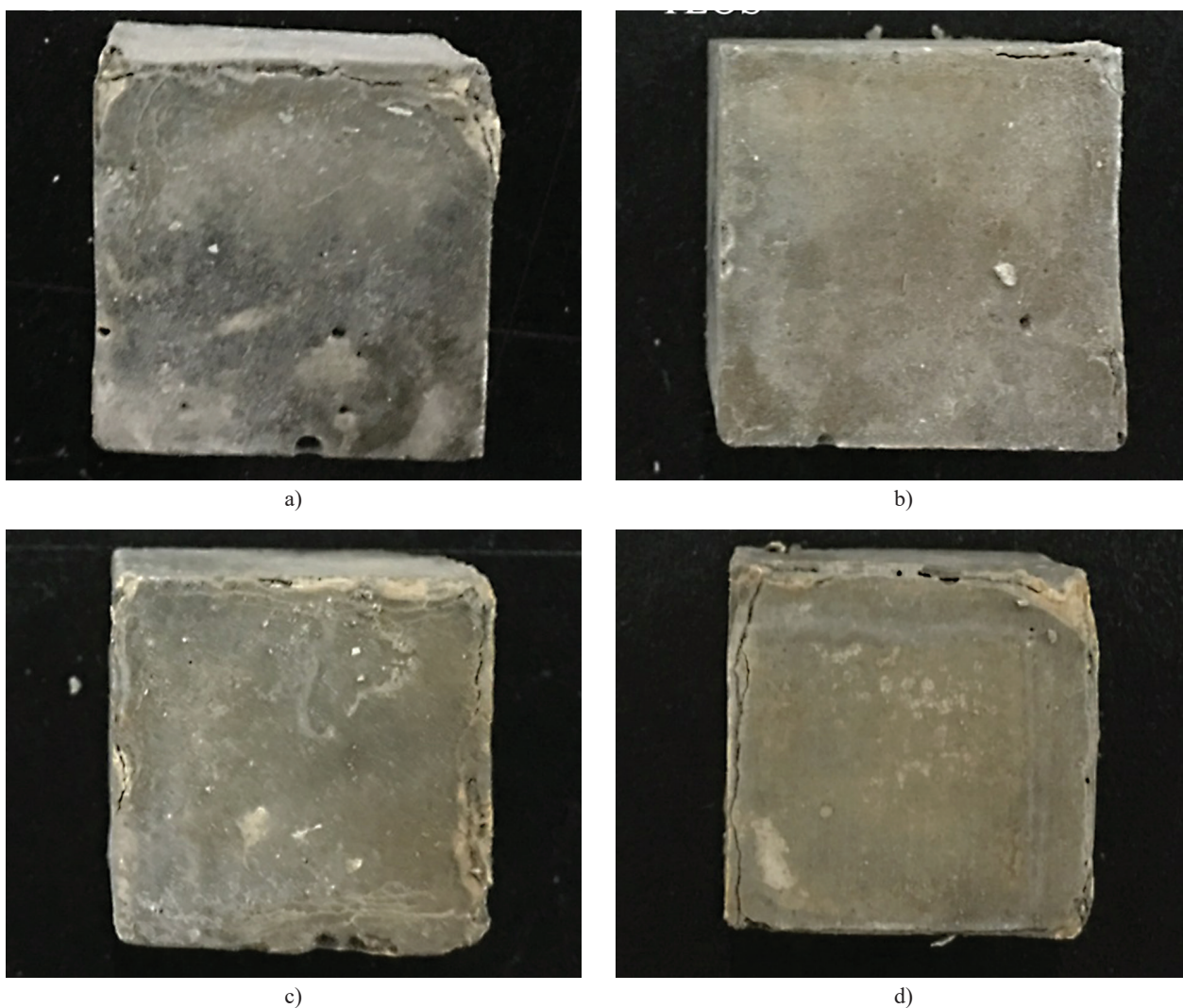

Figure 6. The images of the paste samples cured in 5 % Na_2SO_4 solution for 500 days: a) the control sample and treated by b) TEOS, c) Na_2SiO_3 d) silane).

When the samples were treated at 28 days after casting, all the three agents improve the corrosion resistance of the sample to different degrees: 49 %, 28 % and 24 % higher of the compressive strength is seen in samples cured in Na_2SO_4 solution for 28 days, and corresponding values of 33 %, 13 % and 8 % are seen in the samples cured for 500 days. It shows that the sulfate attack resistance of the three agents follows the order of TEOS, Na_2SiO_3 and silane. The superior performance of the sulfate attack resistance of the TEOS and Na_2SiO_3 treated sample is seen, and this is more obvious in the sodium sulfate solution cured samples for a longer time. This is different from results of the samples cured in the sodium sulfate solution for 7 days, showing that TEOS is more capable of improving the surface quality.

The images of the w/c = 0.4 cement samples that were treated with different agents and immersed in 5 % Na_2SO_4 solution for 500 days are shown in Figure 6. It can be seen that the control sample seriously deteriorates and cracks and spalling is seen on the sample. Similar deteriorations are seen on the Na_2SiO_3 and silane treated samples. For the TEOS treated sample, no obvious deterioration can be seen on the sample surface, implying a superior corrosion resistivity of the sample.

Cracks and spalling of the paste samples immersed in the Na_2SO_4 solution could be mainly due to the expansion that was induced by the reaction of the cement with the Na and SO_4 ions [55]. A reduction of the $Ca(OH)_2$ content as the result of the pozzolanic reaction leads to the formation of the additional C–S–H gel and a compacter microstructure [56]. Figure 7 shows the XRD spectra of the cement paste samples treated by the different agents at 28 days, and the results show that the peak intensity of $Ca(OH)_2$ at c.a., 18° of TEOS treated sample decreases the most when compared with the control sample, indicating its highest degree of the pozzolanic reaction, meaning it has the greatest modification of the physiochemical properties.
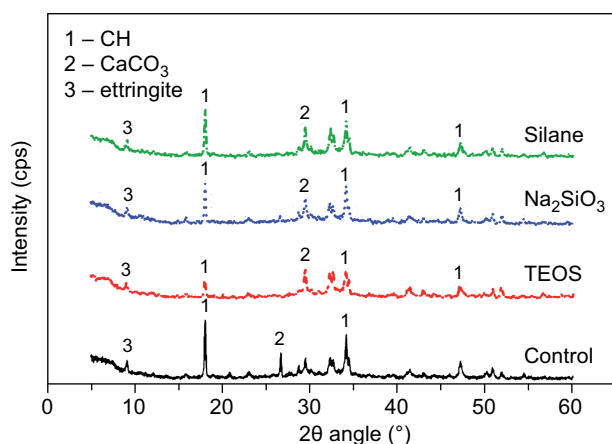
CONCLUSIONS

Based on the comparison of the influences of TEOS, Na_2SiO_3 and silane for the surface treatment of cement-based materials, the effectiveness of the different surface treatment agents are as follows:

- TEOS and silane showed a negative effect for the compressive strength gain and the sulfate attack resistance when applied on the sample of an early age (1 d old).
- TEOS reduces the surface deterioration of the cement-based materials in a sulfate environment, as well as reducing the carbonisation degree of the sample.
- Na_2SiO_3 is beneficial in increasing the sulfate attack resistance of the cement-based materials at both the early and late ages. While TEOS shows a superior sulfate attack resistance performance than Na_2SiO_3 when applied on the sample of a late age (28 days).
- Silane is the most beneficial in reducing the water absorption rate. It shows good performance for the chloride resistance/sulfate attack resistance at an early/late age, but its effect is smaller than those of TEOS and Na_2SiO_3.

REFERENCES

1. Samad S., Shah A. (2017): Role of binary cement including Supplementary Cementitious Material (SCM), in production of environmentally sustainable concrete: A critical review. *International Journal of Sustainable Built Environment*, *6*(2), 663-674. doi: 10.1016/j.ijsbe.2017.07.003

2. Burrows R. W., Kepler W. F., Hurcomb D., Schaffer J., Sellers J. G. (2004): Three simple tests for selecting low-crack cement. *Cement and Concrete Composites*, *26*(5), 509-519. doi: 10.1016/S0958-9465(03)00066-0

3. Zhang P., Wittmann F. H., Vogel M., Müller H. S., Zhao T. (2017): Influence of freeze-thaw cycles on capillary absorption and chloride penetration into concrete. *Cement and Concrete Research*, *100*, 60-67. doi: 10.1016/j.cemconres.2017.05.018

4. Aye T., Oguchi C. T. (2011): Resistance of plain and blended cement mortars exposed to severe sulfate attacks. *Construction and Building Materials*, *25*(6), 2988-2996. doi: 10.1016/j.conbuildmat.2010.11.106

Figure 7. The XRD spectra of the samples treated by the different treatment agents at 28 days and then cured 28 days.

5. Zhang M.H., Chen J., Lv Y., Wang D., Ye J. (2013): Study on the expansion of concrete under attack of sulfate and sulfate–chloride ions. *Construction and Building Materials*, *39*, 26-32. doi: 10.1016/j.conbuildmat.2012.05.003

6. Haynes H., Bassuoni M. T. (2011): Physical salt attack on concrete. *Concrete International*, *33*(11), 38-42.

7. Dai J. G., Akira Y., Wittmann F. H., Yokota H., Zhang P. (2010): Water repellent surface impregnation for extension of service life of reinforced concrete structures in marine environments: the role of cracks. *Cement and Concrete Composites*, *32*(2), 101-109. doi: 10.1016/j.cemconcomp. 2009.11.001

8. Hwang C. L., Young J. F. (1984): Drying shrinkage of portland cement pastes Microcracking during drying. *Cement and Concrete Research*, *14*(4), 585-594. doi: 10.1016/0008-8846(84)90136-4

9. Bisschop J., Van Mier J. G. M. (2002): Effect of aggregates on drying shrinkage microcracking in cement-based composites. Materials and Structures, 35(8), 453-461. doi: 10.1007/BF02483132

10. Du, X., Jin, L., Zhang, R., & Li, Y. (2015). Effect of cracks on concrete diffusivity: a meso-scale numerical study. *Ocean Engineering*, *108*, 539-551. doi: 10.1016/j. oceaneng.2015.08.054

11. Wu Z., Wong H. S., Buenfeld N. R. (2017): Transport properties of concrete after drying-wetting regimes to elucidate the effects of moisture content, hysteresis and microcracking. *Cement and Concrete Research*, *98*, 136-154. doi: 10.1016/j.cemconres.2017.04.006

12. Bazant Z.P., Sener S., Kim J. K. (1987): Effect of cracking on drying permeability and diffusivity of concrete. *Materials Journal*, *84*(5), 351-357.

13. Samaha H. R., Hover K. C. (1992): Influence of micro-cracking on the mass transport properties of concrete. *Materials Journal*, *89*(4), 416-424.

14. Pan X., Shi C., Zhang J., Jia L., Chong L. (2018): Effect of inorganic surface treatment on surface hardness and carbonation of cement-based materials. *Cement and Concrete Composites*, *90*, 218-224. doi: 10.1016/j.cemconcomp. 2018.03.026

15. Wu Z., Wong H. S., Buenfeld N. R. (2015): Influence of drying-induced microcracking and related size effects on mass transport properties of concrete. *Cement and Concrete Research*, *68*, 35-48. doi: 10.1016/j.cemconres.2014.10.018

16. Cui Z., Alipour A. (2018): Concrete cover cracking and service life prediction of reinforced concrete structures in corrosive environments. *Construction and Building Materials*, *159*, 652-671. doi: 10.1016/j.conbuildmat.2017. 03.224

17. Zhu Y. G., Kou S. C., Poon C. S., Dai J. G., Li, Q. Y. (2013): Influence of silane-based water repellent on the durability properties of recycled aggregate concrete. *Cement and Concrete Composites*, *35*(1), 32-38. doi: 10.1016/j.cemcon-comp.2012.08.008

18. Cui G., Liu J., Chen C., Li C.F., Shi L. (2012). Study on silane impregnation for protection of high performance concrete. *Procedia Engineering*, *27*, 301-307. doi: 10.1016/ j.proeng.2011.12.456

19. Kagi D. A., Ren K. B. (1995): Reduction of water absorption in silicate treated concrete by post-treatment with cationic surfactants. *Building and Environment*, *30*(2), 237-243. doi: 10.1016/0360-1323(94)00047-V

20. Almusallam A. A., Khan F. M., Dulaijan S. U., Al-Amoudi O. S. B. (2003): Effectiveness of surface coatings in improving concrete durability. *Cement and Concrete Composites*, *25*(4-5), 473-481. doi: 10.1016/S0958-9465 (02)00087-2

21. Medeiros M. H., Helene P. (2009): Surface treatment of reinforced concrete in marine environment: Influence on chloride diffusion coefficient and capillary water absorption. *Construction and Building Materials*, *23*(3), 1476-1484. doi: 10.1016/j.conbuildmat.2008.06.013

22. Pan X., Shi Z., Shi C., Ling T. C., Li N. (2017): A review on surface treatment for concrete–Part 2: Performance. Construction and Building Materials, 133, 81-90. doi: 10.1016/j.conbuildmat.2016.11.128

23. Basheer P. A. M., Basheer L., Cleland D. J., Long A. E. (1997): Surface treatments for concrete: assessment methods and reported performance. *Construction and Building Materials*, *11*(7-8), 413-429. doi: 10.1016/S0950-0618(97) 00019-6

24. Sanchez L. F. M., Fournier B., Jolin M., Mitchell D., Bastien J. (2017): Overall assessment of Alkali-Aggregate Reaction (AAR) in concretes presenting different strengths and incorporating a wide range of reactive aggregate types and natures. *Cement and Concrete Research*, *93*, 17-31. doi: 10.1016/j.cemconres.2016.12.001

25. Sandrolini F., Franzoni E., Pigino B. (2012): Ethyl silicate for surface treatment of concrete–Part I: Pozzolanic effect of ethyl silicate. *Cement and Concrete Composites*, *34*(3), 306-312. doi: 10.1016/j.cemconcomp.2011.12.003

26. Sanchez M., Alonso M. C., González R. (2014): Preliminary attempt of hardened mortar sealing by colloidal nanosilica migration. *Construction and Building Materials*, *66*, 306-312. doi: 10.1016/j.conbuildmat.2014.05.040

27. Cai Y., Hou P., Duan C., Zhang R., Zhou Z., Cheng X., Shah S. (2016): The use of tetraethyl orthosilicate silane (TEOS) for surface-treatment of hardened cement-based materials: A comparison study with normal treatment agents. *Construction and Building Materials*, *117*, 144-151. doi: 10.1016/j.conbuildmat.2016.05.028

28. Franzoni E., Pigino B., Pistolesi C. (2013): Ethyl silicate for surface protection of concrete: performance in comparison with other inorganic surface treatments. *Cement and Concrete Composites*, *44*, 69-76. doi: 10.1016/j.cemconcomp. 2013.05.008

29. Feng H., Le H. T. N., Wang S., Zhang M. H. (2016): Effects of silanes and silane derivatives on cement hydration and mechanical properties of mortars. *Construction and Building Materials*, *129*, 48-60. doi: 10.1016/j.conbuildmat. 2016.11.004

30. Kong X. M., Liu H., Lu Z. B., Wang D. M. (2015): The influence of silanes on hydration and strength development of cementitious systems. *Cement and Concrete Research*, *67*, 168-178. doi: 10.1016/j.cemconres.2014.10.008

31. De Vries J., Polder R. B. (1997): Hydrophobic treatment of concrete. Construction and Building Materials, 11(4), 259-265. doi: 10.1016/S0950-0618(97)00046-9

32. GB 175-2007, Common Portland cement, 2008.

33. GB/T 50081-2002, Standard for test method of mechanical properties on ordinary concrete, 2003.

34. ASTM C1585-04, Standard Test Method for Measurement of Rate of Absorption of Water by Hydraulic-Cement Concretes, ASTM International, West Conshohocken, PA, 2004.

35. Hou P., Zhang R., Cai Y., Cheng X., Shah S. P. (2016): In situ Ca(OH)₂ consumption of TEOS on the surface of hardened cement-based materials and its improving effects on the Ca-leaching and sulfate-attack resistivity. *Construction and Building Materials*, *113*, 890-896. doi: 10.1016/j.conbuildmat.2016.03.155

36. GB/T 50082-2009, Standard for test methods of long-term performance and durability of ordinary concrete, 2010.

37. Pan X., Shi Z., Shi C., Ling T. C., Li N. (2017): A review on concrete surface treatment Part I: Types and mechanisms. *Construction and Building Materials*, *132*, 578-590. doi: 10.1016/j.conbuildmat.2016.12.025

38. Mijarsh M. J. A., Johari M. M., Ahmad Z. A. (2015): Effect of delay time and Na₂SiO₃ concentrations on compressive strength development of geopolymer mortar synthesized from TPOFA. *Construction and Building Materials*, *86*, 64-74. doi: 10.1016/j.conbuildmat.2015.03.078

39. Mehta P.K., Monteiro P.J. (2006). *Concrete: Microstructure, Properties, and Materials.* McGraw-Hill, New York.

40. Attanayake U., Liang X., Ng S., Aktan H. (2006): Penetrating sealants for concrete bridge decks—selection procedure. *Journal of Bridge Engineering*, *11*(5), 533-540. doi: 10.1061/(ASCE)1084-0702(2006)11:5(533)

41. Franzoni E., Varum H., Natali M. E., Bignozzi M. C., Melo J., Rocha L., Pereira E. (2014): Improvement of historic reinforced concrete/mortars by impregnation and electrochemical methods. *Cement and Concrete Composites*, *49*, 50-58. doi: 10.1016/j.cemconcomp.2013.12.013

42. Lutomirska M., Lutomirski S. (2014): Comparison of Damage due to Corrosion for Reinforced Concrete Tanks for Raw and Treated Water. *Procedia Engineering*, *91*, 244-249. doi: 10.1016/j.proeng.2014.12.054

43. Liu J., Ou G., Qiu Q., Chen X., Hong J., Xing F. (2017) : Chloride transport and microstructure of concrete with/without fly ash under atmospheric chloride condition. Construction and Building Materials, 146, 493-501. doi: 10.1016/j.conbuildmat.2017.04.018

44. Isteita M., Xi Y. (2017): The effect of temperature variation on chloride penetration in concrete. *Construction and Building Materials*, *156*, 73-82. doi: 10.1016/j.conbuildmat.2017.08.139

45. Homan L., Ababneh A. N., Xi Y. (2016): The effect of moisture transport on chloride penetration in concrete. *Construction and Building Materials*, *125*, 1189-1195. doi: 10.1016/j.conbuildmat.2016.08.124

46. Martin III W. D., Kaye N. B., Putman B. J. (2014): Impact of vertical porosity distribution on the permeability of pervious concrete. *Construction and Building Materials*, *59*, 78-84. doi: 10.1016/j.conbuildmat.2014.02.034

47. Neithalath N., Sumanasooriya M. S., Deo O. (2010): Characterizing pore volume, sizes, and connectivity in pervious concretes for permeability prediction. *Materials Characterization*, *61*(8), 802-813. doi: 10.1016/j.matchar.2010.05.004

48. Huang, H., Gao, X., Wang, H., & Ye, H. (2017). Influence of rice husk ash on strength and permeability of ultra-high performance concrete. *Construction and Building Materials*, *149*, 621-628. doi: 10.1016/j.conbuildmat.2017.05.155

49. Li X., Xu Q., Chen S. (2016): An experimental and numerical study on water permeability of concrete. *Construction and Building Materials*, *105*, 503-510. doi: 10.1016/j.conbuildmat.2015.12.184

50. Zhou C., Ren F., Wang Z., Chen W., Wang W. (2017): Why permeability to water is anomalously lower than that to many other fluids for cement-based material?. *Cement and Concrete Research*, *100*, 373-384. doi:10.1016/j.cemconres.2017.08.002

51. Pigino B., Leemann A., Franzoni E., Lura P. (2012): Ethyl silicate for surface treatment of concrete–Part II: Characteristics and performance. *Cement and concrete composites*, *34*(3), 313-321. doi: 10.1016/j.cemconcomp.2011.11.021

52. Thompson J. L., Silsbee M. R., Gill P. M., Scheetz B. E. (1997): Characterization of silicate sealers on concrete. *Cement and Concrete Research*, *27*(10), 1561-1567. doi: 10.1016/S0008-8846(97)00167-1

53. Wittmann F. H., Zhao T. J., Ren Z. J., Guo P. G. (2009): Influence of surface impregnation with silane on penetration of chloride into cracked concrete and on corrosion of steel reinforcement. *International Journal of Modelling, Identification and Control*, *7*(2), 135-141. doi: 10.1504/IJMIC.2009.027066

54. Shi Z., Shi C., Liu H., Li P. (2016): Effects of triisopropanol amine, sodium chloride and limestone on the compressive strength and hydration of Portland cement. *Construction and Building Materials*, *125*, 210-218. doi: 10.1016/j.conbuildmat.2016.08.030

55. Santhanam M., Cohen M. D., Olek J. (2003): Mechanism of sulfate attack: a fresh look: Part 2. Proposed mechanisms. *Cement and Concrete Research*, *33*(3), 341-346. doi: 10.1016/S0008-8846(02)00958-4

56. Taylor H.F. (1997). *Cement Chemistry.* Thomas Telford.