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Bc. Valeriia Iliushchenko



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SURFACE TREATMENT OF CEMENTITIOUS SYSTEMS BY SILICATE SEALERS

POVRCHOVÉ OŠETŘENÍ CEMENTOVÝCH SYSTÉMŮ VYBRANÝMI ROZTOKY
KŘEMIČITANŮ

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DIPLOMOVÁ PRÁCE

AUTHOR

AUTOR PRÁCE

Bc. Valeriia Iliushchenko

SUPERVISOR

VEDOUCÍ PRÁCE

Ing. Lukáš Kalina, Ph.D.

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Bc. Valeriia Iliushchenko
Student



Ing. Lukáš Kalina, Ph.D.
Head of thesis



doc. Ing. František Šoukal, Ph.D.
Head of institute



prof. Ing. Martin Weiter, Ph.D.
Dean

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ABSTRACT

Silicate-based impregnations are widely used for to protect concrete against the aggressive environment. Nevertheless, understanding of the several aspect concerning to this type of impregnation is not entirely clear. This thesis presents the information about individual properties of selected silicates, more precisely potassium, sodium, lithium silicates and colloidal silica, then effectiveness in terms of water absorption, degree the effect on cement hydration, the ability of these agents to close pores and the influence on the microstructure of the cement substrate as well as penetration capability. The effectiveness of film-forming substances was assessed both on fresh cement and on more hydrated ones, applied after 1 hour and 24 hours after mixing the mixture, respectively. Instrumental methods such as mercury porosimetry, rheometry, isothermal calorimetry, X-ray diffractometry and scanning electron microscopy were used to achieve quality results. Considering to the tests performed, a certain effectiveness of the care agents was proved. The results of all tests showed a higher efficiency of these substances in the case of treatment on a more hydrated cement surface, which was probably due to a higher degree of hydration resulting in the creation of new phases with which silicates were able to react and in some way affect the microstructure.

KEY WORDS

Concrete sealers, treatment, potassium silicate, sodium silicate, lithium silicate, colloidal silica, calcium silicate hydrate (C-S-H gel)

ABSTRAKT

Impregnace na bázi silikátů se široce používá k ochraně betonu před agresivním prostředím. Pochopení aspektů týkajících se tohoto typu impregnace však není zcela jasné. Tato práce představuje informaci o jednotlivých vlastnostech vybraných křemičitanů, přesněji draselného, sodného, lithného a koloidního oxidu křemičitého (koloidní silika), dále o účinnosti z hlediska nasákavosti, stupni účinku na hydrataci cementu, schopnosti těchto látek uzavřít póry a jejich vliv na mikrostrukturu cementového substrátu a na penetrační schopnost. Účinnost filmotvorných látek byla hodnocena jak na čerstvém cementovém tmelu, tak na vyzrálém, aplikovaných po 1 a 24 hodinách od smíchání směsi. K dosažení kvalitativních výsledků byly použity instrumentální metody, jako je rtuťová porosimetrie, rheometrie, izotermální kalorimetrie, rentgenová difrakční analýza a skenovací elektronová mikroskopie. S ohledem na provedené testy byla prokázána určitá účinnost ošetřujících přísad. Výsledky všech testů ukázaly vyšší účinnost těchto látek v případě ošetření na vyzrálém cementovém povrchu, což bylo pravděpodobně způsobeno vyšším stupněm hydratace, díky čemuž se vytvořily nové fáze, se kterými silikáty byly schopné zareagovat a jistým způsobem ovlivnit mikrostrukturu.

KLÍČOVÁ SLOVA

Betonové sealery, ošetření, křemičitan draselný, křemičitan sodný, křemičitan lithný, koloidní oxid křemičitý, kalcium-silikátový-hydrát (C-S-H gel)

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DECLARATION

I declare that I have written my master's thesis on the theme of "Surface treatment of cementitious system by silicate sealers" independently, under the guidance of the master's thesis supervisor. All used technical and others literature was cited without infringing copyright and is listed at the end of the thesis.

Brno _____

(author's signature)

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1 INTRODUCTION

Nowadays population is growing, more and more factories and vehicle are building, it is means, that the quality of the environment worsen and not only all of us are exposed to the aggressive conditions of the air, water, ground, but and facilities around us like buildings and bridges either. Many of these facilities are made from the concrete. The concrete is admired for its weight and durability. That is why it serves as the foundation of modern life, holding time, nature, the elements and entropy at bay. When combined with reinforcement like steel, it is the material that ensures our tower blocks do not fall, our dams do not burst, our roads to be not bend and our electricity grid remains connected. The basic component of the concrete constructions is cement. The cement surface represents the porous system, which contains micro-pores, micro-cracks, micro-voids, amongst the other defects, which provide easy path for the undesirable penetration of water and water-dissolves destructive solutions like chlorides, sulphur dioxide, carbon dioxide and sulphates. These aggressive substances could be harmful for the concrete structure or for the reinforcement. Aggressive salts are transported through the pores and degrade the structure of the concrete, which can result in the construction collapsing.

A commonly used method of eliminating the permeability of these structures is to reduce the porosity of the material (e.g. reducing the water content, adding special ingredients etc.), but the problem is that this method is not applicable to existing buildings.

The surface treatments of concrete structures are offered to reduce the risk of deterioration of these structures and, conversely, serve as protective agents to increase durability. Depending on the chemical composition, these substances can be divided into two groups: organic and inorganic. Each of these groups has their stronger and weaker sides. Organic materials generally have good surface properties but are less stable in terms of durability in comparison with inorganic materials. In addition, organic substances are volatile and not eco-friendly. At the same time, inorganic materials are more stable and less burdensome for the environment. In case of organic treatment agents, they interact with the concrete surface as a coating, sealers and pore liners. These types of treatment mechanism do not ensure pore filling, they either form the continuous film or cover the pore surface. Among the organic treatment belong polymer resins, silanes and siloxanes.

Beyond, the inorganic agents are considered as pore blockers, that completely or partially fill open pores of the material due to the reaction of with the substrate surface. The main represents of the inorganic treatment agents are silicate sealers.

This paper deals with the efficiency of the inorganic treatment agents, mechanism of the reaction and the way of the application on the substrate surface. Three types of alkaline silicate sealers (other words – water glasses) and one type of colloidal silica have been chosen as the inorganic surface treatment agents. The individual properties if the treatment substances have been tested by using inductive titration, X-ray diffractometry and rheometry. Then, have been studied the influence of treatment agents to the cement surface by using chemical analysis as isothermal calorimetry, mercury porosimetry and electron scanning microscopy and also mechanical properties using e.g. strength measurement (flexural and compressive).

2 GOALS AND OBJECTIVES OF THE THESIS

This thesis is focused on the study the effects and mechanism of alkali silicates and colloidal silica on cement substrates, including optimization of the application time. Compliance with the following partial goals is fundamental to achieve the aim of the thesis:

- A preparation of the testing samples following by treatment process;
- Studying the properties of the individual treatment agents;
- Evaluation of the effect of treatment on the properties of the cement substrate;
- Characterization of the surface treatment by selected analytical methods;
- Comparing the degree of effect of the treatment substances with each other.

3 THEORETICAL BACKGROUND

This chapter provides basic information about materials that was used in practical part as well as their properties are discussed. The first part is devoted to the insight into the traditional treatment of polymeric materials. Then the mechanisms of interaction of coatings with the cement surface will be described. Further part carries out the information about inorganic treatment agents and a brief review of the previous studies. Finally, the interaction of alkali silicates with the hydration products of the cement substrate will be solved in more detail.

3.1 Surface treatment

Nowadays concrete is the second widely used material on the Earth. Concrete is the basic material that used is building industry. We can find it in every industry we think of, constructions of buildings, industrial facilities and social overhead capital. The concrete is the basis of modern life due to its durability and steadiness [1].

In recent decades the problem of deterioration of concrete structures has become more and more current for different countries in the world [2]. The durability of concrete is one of the social problems due to its deterioration in the various environment. The mechanisms of degradation and damage of structures have been described in the literature [3]. Durability is primarily driven by the composition and quality of the surface layer. One of the possible reasons for reducing the durability of concrete structures is the relatively high permeability of concrete to gases and liquids [3]. Fast-growing cities and newly built factories make environmental pollution more and more aggravating. So that currently concrete constructions are exposed to raucous physical and chemical environments. One of the ways how to delay the degradation and to increase durability of concrete construction is to reduce the porosity. There are several ways how to reduce porosity: reduce water to concrete ratio or by using chemical admixtures. The disadvantage of these methods is that it is impossible to implement them on already constructed structures. The effect of porosity decreasing is shown in fig. 1.

One of the solutions how to prevent penetration of substances through concrete structures (without adjusting the composition of the mixture) is to use treatment agents on the surface of concrete structures, floors, etc. [4][5].

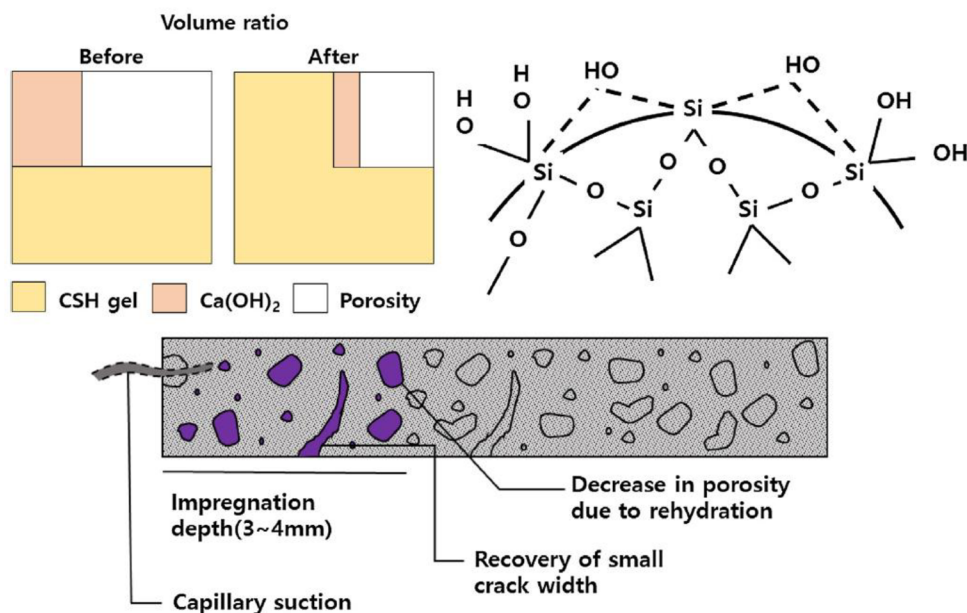


Figure 1 Schematic representation for surface impregnation [6]

To prevent premature degradation, it is needed to use surface coating. According to composition, coating materials are divided into organic and inorganic. The most commonly-used treatment is organic surface. On the one hand organic treatment has a distinctive better protective effect. On the other hand, organic surface treatment is not such an ecology friendly, is poor fire resistant, susceptible to cracking, has a limited lifetime and difficult to remove after loss of protective function.

The most common representative of inorganic surface treatment, also alkaline silicate, in other words ‘water glass’ (WG) is sodium silicate. Also, but less used potassium silicate, lithium silicate and fluorosilicate as a surface treatment agent. Although inorganic materials show better durability, it has not been yet devoted much attention to this area of research, in particular interaction and reaction with concrete surface and depth of penetration. Depending on the effect and interaction with the surface substrate, surface treatments can be divided into three types, according to the EN 1504-2 [7] (fig. 2): a (a) hydrophobic impregnation that forms a film capable of repelling water but does not fill the entire pore space, (b) impregnation that entire or partial fills the pores and finally a (c) film-forming sealing that forms a continuous protective layer along the whole concrete surface [8][9][10][11].

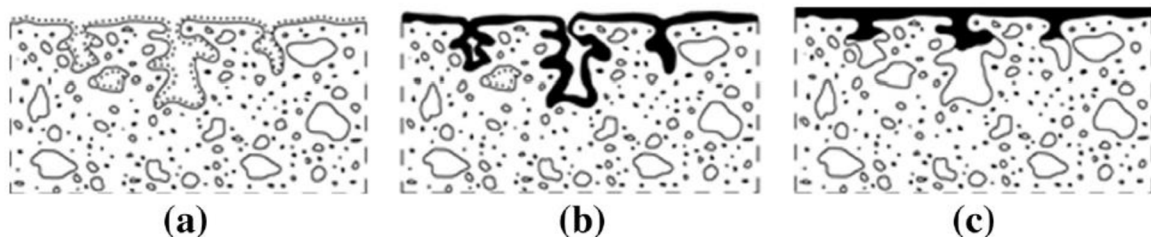


Figure 2 Types of surface treatment a) pore liners b) coating c) pore blockers [2]

Some of these coatings are capable of penetrating inwardly and reacting with cementitious products, thereby reducing porosity and increasing the surface strength. In some cases, the formed continuous film serves as a barrier at the cement surface from the environmental factors [2].

In recent years, the most commonly used impregnating agents are compounds based on silanes and siloxanes (water repellents) and on silicate bases (pore blockers, known as WG). The essence of the first type of impregnation is the formation of a thin hydrophobic layer on the surface, while in the case of silicate, a chemical reaction occurs between the treatment agent and the concrete surface, thereby strengthening the surface.

Despite the fact that silicate-based compounds are popular for treatment, the literature review shows (chapter 3.2) that these substances are not yet fully investigated and therefore, attention is paid to them. The following subchapters provide information about several types of organic treatment agents and more detailed mechanism of their interaction with the concrete surface.

3.1.1 Organic treatment agents

Epoxy resins, acrylates and polyurethanes are considered as traditional protective materials, which have been used for many years in building industry. Properties of these polymer coating agents are shown in tab. 1.

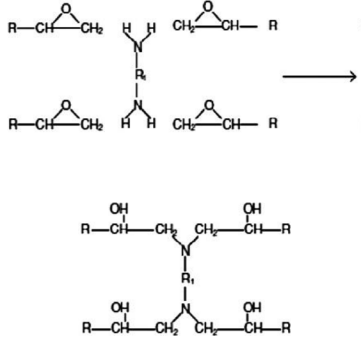
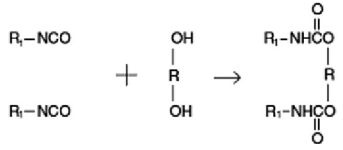
Epoxy resins have better adhesion to concrete surface, unlike acrylic acid, but acrylic acid in its range has better alkali resistance and weathering. Polyurethanes have better effect in protecting concrete without shrinkage. They have a high resistance against acid attack;

however, they are non-stable in high alkaline environment. Moreover, main monomers of polyurethane, isocyanates, are harmful and dangerous for human health [12][13].

The main problems at the polymer coating/concrete interface are cracking, blistering, holes and peeling. Blistering may result in loss of adhesion due to osmotic pressure. Volume shrinkage of the treatment can cause cracking agent due to temperature changes or cracking of the cementitious substrate. The coating layer can even cause holes and pores which can then increase the permeability. The peeling is caused by the loss of adhesion of the coating to the cementitious surface and this can induce penetration of aggressive substances between the polymeric agent and the cementitious substrate.

Less traditional organic treatment agents are silanes (i), siloxane oligomers (ii) and mixtures of these two materials [14].

Table 1 Properties of traditional polymer treatment agents [12]

Agent	Curing mechanism	Advantages	Disadvantages
Epoxy resin		<p>Easy to cure; Low shrinkage; Good adhesive strength; Good chemical resistance.</p>	<p>Low fracture energy; Low impact to strength; Poor hydrophobicity; Low thermal stability; Poor resistance to the initiation and propagation of cracks.</p>
Acrylic	Physically drying	<p>High resistance to hydrolysis and ultraviolet radiation; Good alkali resistance.</p>	<p>Low bond strength; Poor ductility; Generally not applied for constant immersion in water of soil.</p>
Polyurethane		<p>Excellent resistance to weathering; Self-healing; No shrinkage.</p>	<p>Poor resistance towards mechanical strains and deformation and/or degradation at high temperature.</p>

i) *Silanes*

Silanes are colourless hydrophobic materials which are chemically known as an alkyl trialkylalkoxisilane. Due to their small size, $1.0 \cdot 10^{-6} - 1.5 \cdot 10^{-6}$ mm in diameter, allows them to penetrate in high dense surface. Commercial products are generally in highly concentrated solution (about 20 wt. %) and reacts with silica-based materials or alumina. Silanes are very volatile compounds due to reduced molecular structure. The structure of silane is shown in fig. 3 [15].

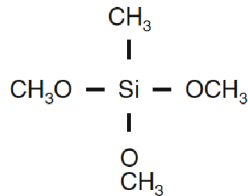


Figure 3 Structure of silane [14]

ii) *Siloxanes*

Siloxanes are colourless treatment substances, chemically known as alkylalkoxisiloxanes. Despite the fact that siloxanes have larger molecules (diameter is about $1.5 \cdot 10^{-6} - 7.5 \cdot 10^{-6}$ mm) compared to silanes, it is still acceptable to penetrate to concrete substrate. High chemical reactivity with alumina-silica-based substrates guarantees long durability and high rate of hydrophobicity of the concrete surface. In that way the treated hydrophobic surface has durability of over 10 years and is not easy to remove. An advantage of siloxanes is that they can be applied on moist surface and are less volatile. The structure of siloxane is shown in fig. 4 [14].

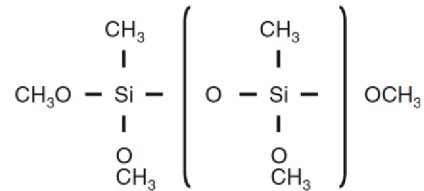


Figure 4 Structure of siloxane [14]

In general, silanes and siloxanes have the similar mechanism of reaction with the substrate surface. First of all, they penetrate to concrete pores, then form hydrophobic layer, thereby protect surface from water penetration, but allow water vapour to enter or exit, what is enable concrete material to breathe [16].

The mechanism of interaction between the hydrophobic agent and substrate is illustrated in fig. 5.

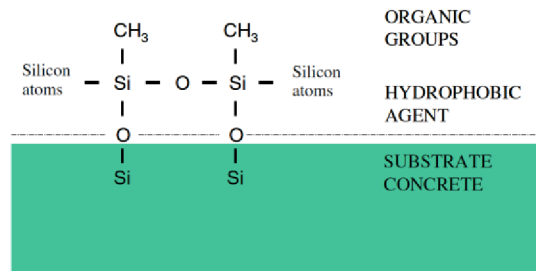


Figure 5 Mechanism of interaction between the hydrophobic agent and concrete surface [14]

Generally, traditional polymer treatment agents are belonged to the group of coatings, whereas silanes and siloxanes are considered as pore liners. More detailed mechanisms of interaction with concrete surface is written in following two subchapters (3.1.2 and 3.1.3.).

3.1.2 *Coatings and sealers*

Providing a physical barrier on the concrete surface can be done by treatment the surface with a coating or sealant to protect it from the action of aggressive environmental agents. Coatings can only be applied to a homogeneous and smooth surface with pore widths of maximum 0.1 mm. Therefore, sealers are able to cover cracks of 0.1 mm wide. In case that a concrete structure breaks after coating application, the whole film breaks. It is not possible to apply a coating to a wet surface, as the internal vapour pressure of moisture can cause bubbles and film quality to deteriorate [12]. The most common representatives of this group are shown and briefly described in the following chapter 3.1.3.

3.1.3 *Pore liners (hydrophobic treatment)*

The use of a hydrophobic coating on concrete surface has been proven to minimize moisture transfer, thereby increasing its durability and extending its service life. Jacob and Herman in their work in 1998 showed that at least for 10 years hydrophobic agents can be effective in case that agent was applied on the 6-month-old surface. The authors have also shown that the effectiveness of the hydrophobic agent applied to fresh surfaces is very low. Surface have to be at least 28-days old or older because of hydration process, which has to be almost completed. One of the common materials for the care of concrete structures are silanes, siloxanes and mixture of these two components. Due to small molecular size they can easily penetrate concrete pores. It works by the following mechanisms. This is a capillary suction process that is an unsaturated transport process which is controlled by capillary forces. Capillary force is a function of surface tension σ of the wetting liquid and its contact angle θ with a pore of a radius r . Capillary force is defined by following Young-Laplace equation (1) [13]:

$$\Delta P = \frac{2 \cdot \sigma \cdot \cos\theta}{r} \quad (1)$$

From the thermodynamic point of view, if the angle $q < 90^\circ$ thus falls, the molecular attraction between the liquid and the substrate and formation of capillary rise and concave meniscus occurs. Conversely, if the angle $q > 90^\circ$, it causes a water-repellent layer to prevent moisture ingress. It is this effect that can be achieved by using silanes to treat concrete constructions. Both of these effects are illustrated below in fig. 6 [2].

The hydrophobic treatment agents are susceptible to the ultraviolet (UV) radiation. Nevertheless, only the surface is affected to the UV rays and cannot penetrate the concrete substrate. As a result, the minimum amount of the penetrated hydrophobic agent is essential for obtaining a high effective water repellent effect. It is easy to control and achieve the required depth of penetration on porous substrates, such as ceramic bricks, which is not the case with a concrete surface, which is characterized by much lower porosity. Also, more resistant and denser concretes require special methods to produce a protective surface that would be able to penetrate into small pores.

From the report 244 of the ‘National Cooperative Highway Research Program’ the USA recommends the use of surface protection systems that reduce water absorption by 75 %, compared to concrete without treatment protection. The ‘German Committee for Reinforced Concrete’ defined the absorption reduction by 50 % [17][18].

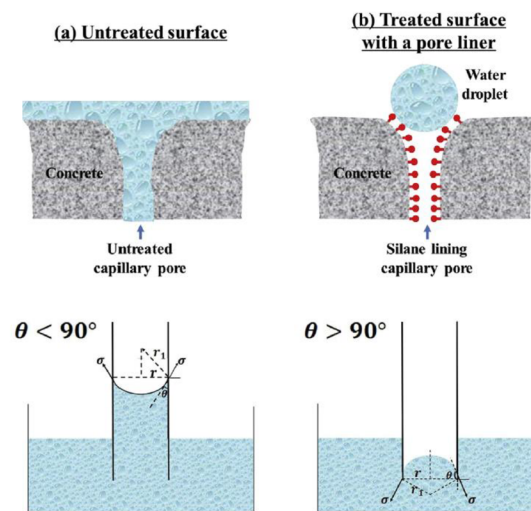


Figure 6 Illustration of silanes effect [13]

Since 1986 in the United Kingdom a hydrophobic agent isobutyltrimetoxysilane was applied to bridges constructions against chloride penetration. According to the United Kingdom, many companies in the United States and the Department of Transportation in Germany started to use hydrophobic agents to bridges structures to prevent chloride attack. The Netherlands were joined by the above-mentioned states, where Ministry of Transportation started to use hydrophobic agent to different concrete surfaces to protect constructions against aggressive environment [14].

3.2 Inorganic treatment agents

This chapter provides information about representatives of inorganic treatment agents.

3.2.1 Short review of inorganic coatings

Thompson et al. [19] are among the first who studied the effectiveness of a silicate-based coating. In their work, authors investigated the efficacy of two different solutions of sodium silicate with the same silicate modulus (3.22) but different dry matter content (37.6 wt. % and 38.6 wt. %). The tests were carried out on both commercial paving blocks made by cement paste prepared in the laboratory with the water-cement ratio (w/c) of 0.48. After testing for wear resistance, water penetration, and chloride permeability, the authors concluded that the effectiveness of the sodium silicate solution was low.

Ibrahim et al. [20] compared the performance of various agents (silane, silane/siloxane, silane/siloxane with acrylic additive, silicone resin solution and sodium silicate) against the deterioration of concrete quality (w/c ratio was 0.48). The samples were tested in aggressive sulphate environment, carbonation and chloride penetration. The effectiveness of the investigating agents decreased in the council: silane/siloxane with an acrylic topcoat acrylic coating > silane > silane/siloxane > silicone resin solution > sodium silicate. The impregnation of silicate sodium was achieved by a reduction of the carbonation of the concrete after about five weeks by approximately 50 % compared to the reference sample. However, the same result did not succeed in subjecting the samples to the attack of chloride ions, so that a decrease in compressive strength was observed after exposure to the sulphate solution (330 days).

Dai et al. [21] evaluated the productivity of surface treatments on the reinforced concrete structure, which was exposed to the simulated wet subtropical environment. Two sets of

protective surfaces were tested: silane- and sodium silicate-based treatments. The result was that sodium silicate failed to meet the expected hopes. Impregnation on the basis of sodium silicate did not prevent the absorption of water so that chloride anions could penetrate to the reinforcement, which would cause its corrosion.

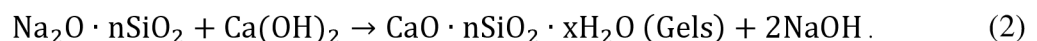
Results of Mirza et al. [22] studies confirm earlier study about poor effectiveness of sodium silicate against water absorption.

In contrast with organic treatment agents, which are not suitable for fresh mixtures [23] inorganic solutions conversely, as Kagi a and Ren [24] writes in their work, are appropriate for the fresh systems. Above mentioned authors [24] in their work studied the influence of sodium silicate to the concrete surface. Concrete, after it has set, contains a small amount of hydrated lime which in time is converted to calcium carbonate by carbon dioxide in the atmosphere. When diluted soluble silicate such as sodium silicate is allowed to impregnate into a concrete surface, the silicate reacts with these calcium compounds and a hard glassy material, consisting mainly of calcium silicate and silica formed in the pores of the concrete. A denser and harder surface layer is produced. In addition to hardening the surface, the silicate treatment reduces the permeability of concrete to water. However, this reduction of permeability to water is not marked and is not equivalent to the reduction achieved by impregnation with, for instance, silicone water repellents. This is due to the hydrophilic property of the silicate structure. A significant resistance of the concrete surface against the penetration of undesirable substances can be achieved by repeatable application of silicates on the fresh concrete surface [24].

However, work the experimental data on the effect of sodium silicate are limited and the mechanism of concrete surface improvement is not quite clear. Generally inorganic surface treatment agents are considered as pore blockers, the mechanism of their effect is described in the following chapter.

3.2.2 Pore blockers

Pore blockers are used to heal open pores in concrete, increasing hardness and decreasing permeability. Among the known substances, the solutions based on lithium silicate, calcium silicate, sodium silicate, potassium silicate and fluorosilicate are the most commonly used. In H.Y. Moon et al. [25] were studied the effect of inorganic mortar treatment on chloride permeability. Due to the reaction of the $[\text{SiO}_4]^{4-}$ ions contained in the treatment solution, which subsequently reacts with the soluble ions contained in the mortar: Ca^{2+} , Mg^{2+} , Al^{3+} , insoluble colloidal silicate is formed. It has been shown that new microstructure is formed which prevents the penetration of chloride ions. Cement mortar has high porosity, so the treatment solution heals these pores and compact the overall microstructure of the material. The most widespread inorganic pore blocker is sodium water glass. Zhongnan S. et al. [26] in their work based on measurements outlined the effect of sodium silicate as a waterproofing agent that will improve compactness of concrete due to reduced micro-pore, micro-void and the size of microcracks in concrete structures. Xiaoying Pan et al. in their works [12][27] have proven that sodium silicate reduces air permeability by 60–75 %. Sodium water glass reacts with the cement paste ions by the following mechanism, equation (2) [13].



The active sodium silicate reacts with the portlandite in the cement matrix to form insoluble high dense calcium silicate hydrate (C-S-H gel), which blocks pores and increases surface durability and hardness. In general, sodium silicates are considered to be pore blockers. Although the interaction of sealers based on sodium silicate is studied, the exact mechanism by which the surface is improved is not entirely clear. There are some theories trying to clarify the

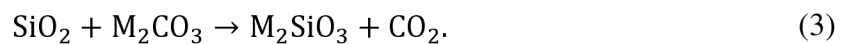
mechanism of action. One of which says that sodium silicate is an effective sealer because the $[\text{SiO}_4]^{4-}$ from water glass will precipitate in the pores of the concrete structure. The second assumption is that the silicates react with an excess of portlandite to form relatively insoluble hydrates of the calcium silicate. Third argument is that silicates make an expansive gel similar to that which is formed during alkali-silicate reaction to fill empty pores [28].

The following paragraphs represents the general information about alkali silicates in the main view and then particular types of the alkali silicates.

Alkali silicate

Generally, silicates are based on $[\text{SiO}_4]^{4-}$ tetrahedra either isolated or as polymers, in which tetrahedra are joined at the corners through bridging oxygen atoms, arranged in chains or sheets or three-dimensional networks. In vitreous silica each tetrahedron is linked to four others, giving a random three-dimensional network without any periodicity or symmetry [29], [30].

Alkali silicates, in other words water glasses (WG) are a set of compounds having the general formula $\text{M}_2\text{O}\cdot n\text{SiO}_2$, where n can take any value and M represents alkali metal ($\text{M} = \text{Na}, \text{K}, \text{Li}$) [31]. The concept of WG was introduced by professor of mineralogy Johann Nepomuk von Fuchs from Munich around 1825 [32]. WG is an aqueous colloidal solution of alkali silicate (sodium, potassium, rarely lithium). That solutions result from the dissolution of the alkali-silica in water. There are two methods of preparation of alkali-silica. The first one is the traditional, which consists in melting quartz sand with the corresponding anhydrous alkali carbonate at temperatures of 1 400 to 1 600 °C (3) which, after rapid cooling, is crushed and subsequently dissolved in water in an autoclave at elevated pressure and temperatures of approximately 140–160 °C [33].



The idea of another method of alkali-silica preparing rests in reciprocal reaction between corresponding alkaline hydroxide and quartz sand. That reaction runs undergo the similar conditions as the traditional method: in an autoclave at elevated pressure and temperature. This method is used largely to prepare alkali-silicate, which are not dissolved in water (lithium silicate).

Generally accepted model for describing the structure of contemporaneous alkali-silicates is the model suggested by Zachariasen-Warren [34]. In this SiO_2 vitreous model, it is presented as a contiguous random network of tetrahedral $[\text{SiO}_4]^{4-}$ connected at the corners (fig. 7).

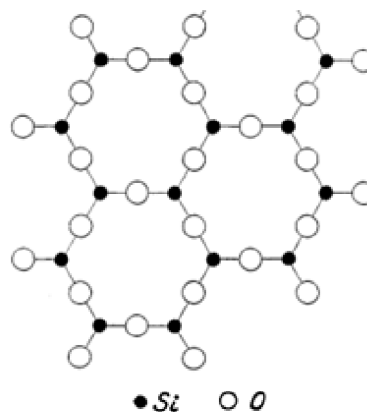


Figure 7 Structure of network of SiO_2 [28]

The random nature of the structure is due to both the distribution of Si-O-Si and dihedral angles among the tetrahedral. The alkali metal cation in the silicate structure serves as a modifier. In the modified network model [34], the addition of one network modifier unit M_2O causes one bridging oxygen atom between two connected tetrahedra to be replaced by two non-bridging oxygen atoms, one in each tetrahedron. The sketch of this structure is shown in fig. 8.

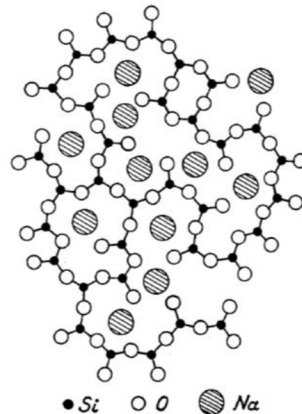


Figure 8 Structure of sodium silica [34]

Composition of WG is characterized by the basic parameter, which is silicate modulus M_s , that means SiO_2/M_2O molar ratio. The parameter can theoretically take any positive values, however in conventional commercially available water glasses it is in the range 0.40–4.1, as the stability of water glasses is limited outside this interval [35], [36]. The main parameter of WG is density, which provides information about the concentration of the solution. The viscosity as well as pH value are also the major parameters. The viscosity of WG depends on its concentration and on the value of the silica module of the starting glass. When comparing viscosity data, it should be taken into account that WG behaves like a Newtonian liquid and therefore the viscosity value depends on the measurement method. The pH is also a function of the chemical composition and the concentration of WG. Water glass, as salt solutions of strong bases and weak acids, are highly alkaline. Represents of alkaline silicates can be sodium silicate, potassium silicate and lithium silicate. Detailed description of these represents is given in following subchapters (i), (ii), (iii). In addition to mentioned alkaline agents, the last subchapter (iv) gives information about nano-silica. The following alkaline silicates and nano-silica are described only from the one of one of a wide range of features – concrete treatment. Physical and chemical properties of these silicates are not defined in detail, they are characterized as a treatment agents and mechanism of their interaction with concrete substrate is represented.

i) *Sodium silicate*

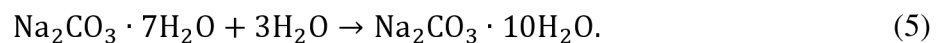
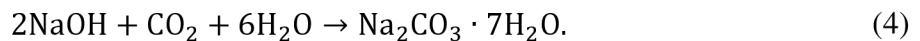
Sodium silicate is also known as a sodium water glass. Firstly, sodium silicate was already used 1930s [37]. The area of using of sodium water glass is very wide: a main raw material in glass production and ceramic industry, admixture to the silicate paint, component of the production of industrial and construction adhesives, impregnation agent in the textile industry, additive to the concrete mixtures, adhesive coating against the moisture. Especially, application of the sodium silicate as an impregnation agent against the moisture and water is crucial in this work.

Impregnation can take place by two mechanisms, either by evaporating of water from water glass or by reaction of silicate with substrate surface resulting in the formation of a solid insoluble gel. Use of a concentrated sodium silicate solution may result in damage to the sample

surface, because formed gel constructs a compact layer, which reduces in volume with the other water loss and the layer can easily detach from the substrate. For this reason, it is necessary to use diluted water glass system. Water glass can be used with inorganic fillers (example: chalk, marble powder) as a solid sealant to glue the ceramics, gypsum and to solidify castings and moulds.

Another way how sodium silicate can fill the capillaries of the concrete surface is that the sodium silicate starts to condense with itself and the substrate in the presence of ambient carbon dioxide (from the atmosphere) to form oligomer or polymer products. These oligomer or polymer products can make a positive contribution to improving the mechanical properties and imparting a waterproof effect to the concrete surface, even if the pores are completely blocked by the siliceous reaction [38].

The benefits of sodium silicates include relatively low cost, but the disadvantage is high reactivity with sample surface. High reactivity prevents sealer penetration into capillaries so reaction carries out just on the surface of the sample. That problem can be solved by opening capillaries (grind surface) or just wet the surface. Another problem with sodium silicate is its tendency to efflorescence. Sodium silicate contains sodium hydroxide, which reacts with carbon dioxide from the air to form soda according to the equations (4) and (5). The process of forming soda is quite slow, has been manifested for many years [39].



Other disadvantages include possible undesirable reactions. Because of high pH of sodium silicate, around 11–12, can arise Alkali-Aggregated Reaction (AAR). In general AAR can be divided into two categories: Alkali-Silica Reaction (ASR) and Alkali-Carbonate reaction (ACR). ASR is the most common kind of AAR, which is found around the world. The problem of ASR is that; it generates 'gel' that swells in present of water. The danger of that 'gel' is that it can cause a volumetric expansion, because of which can lead cracking and then break the material [40][41][42].

ii) Potassium silicate

In general potassium silicates are similar to sodium silicates in their properties, nevertheless, there are some different aspects due to slightly different physical properties. Differences appear as far as application in industry is concerned. Potassium silicate has a higher solubility and compatible with other ingredients. These properties make it possible to use in liquid form: detergents, potassium soaps. Because of greater heat resistance, potassium silicates are used in various high-temperature binders. The reason for the greater heat resistance is the higher softening and creep temperature at the same molar silicon to potassium ratio (unlike to the sodium and silicone). Next advantage of potassium silicate is low probability of efflorescence or carbonate film on surface exposed to the atmosphere. In that reason potassium silicate is suitable in any decorative coatings, ceramic binders, paints, etc. In areas where potassium is an essential component, it can be used in the form of silicate [43].

iii) Lithium silicate

Lithium silicate is the least studied material of the above water glasses. Unlike sodium and potassium silicate, lithium silicate is insoluble in water. Thus, its preparation differs from the traditional preparation, when the silicate powder is dissolved in a hot solution of alkali metal hydroxide. Lithium water glass is prepared by mixing amorphous SiO₂ as a silica sol, with LiOH solution. Initially the suspension has a milky colour, but after a few days of holding it is

turned into a clear lithium water glass solution. In fact, it is a colloidal sol with very fine particles stabilized by Li⁺ ions [44].

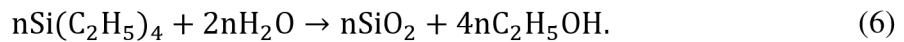
Lithium water glass is widely used in mixtures with zinc powder to protect metal materials from moisture. For better efficiency, lithium water glass is used with sodium. System Li⁺–Na⁺ has better moisture resistance before and after hardening. Lithium silicate has a higher melting point, which implies that after application of lithium water glass to the silica sand surface, the temperature resistance of silica sand increases and it is less fusible.

Lithium water glass comes across a stability problem. Li⁺ ions are too small to form a stable system. Therefore, from a practical point of view, it is advantageous to use a mixed system of potassium, lithium and sodium water glass. The doping of sodium water glass with Li⁺ and K⁺ ions increases bond strength, shelf life and storability [44].

iv) Nano-Silica

One of the latest studies is the application of nano-silica to a concrete surface. Hou et al. in their work [45] proved that due to the fine particle size (up to 100 nm) of the SiO₂ molecule, it exhibits extreme puzzolanic reactivity. In their previous work [46] it turned out reaction rate of nano-SiO₂ is multiply higher than silica fume. Hou's work also reported, that hydration product of nano-SiO₂ are more compact than hydration products of silica fume, which means, that particles of nano-SiO₂ are able to penetrate deeper into the porous structure of concrete.

At present, the sol-gel technique is generally used for the production of nano-SiO₂ on an industrial scale. This technique is based on the condensation and polymerization of SiO₂ monomers formed by hydrolysis of trimethylethoxysilane or tetraethoxysilane (commonly used compounds for the synthesis of nano-silica in a controlled alkaline or acidic environment). The production process can be summarized by equation (6): [47]



The reactivity of alkali silicates is closely related to the formed C-S-H gel in the structure of the cement, it can even modify the structure by incorporating into it. The following chapter is devoted to the structure and origin of C-S-H phases.

3.3 C-S-H phase

Calcium silicate hydrate is the main binding phase in ordinary Portland cement (OPC). Upon interaction with water, the major clinker minerals (tricalcium and dicalcium silicates; C₃S, C₂S) form a hydrosilicate gel (C-S-H) and portlandite (Ca(OH)₂; also, CH, as a by-product). Calcium silicate hydrate is characterized as a poorly crystalline or almost amorphous phase in a fresh cement paste. The exact composition of C-S-H gel is difficult to determine [48][49].

In the form of solid solutions, the C-S-H phase may contain sulfate, aluminum, ferric and alkali ions. The CaO/SiO₂ (C/S) molar ratio depends, inter alia, on the age of the cement paste and generally is in the range of 1.5–1.7 [50].

The average C/S ratio in the fully hydrated C₃S paste can be calculated using the method of the residual Ca(OH)₂ content. This method can also be applied to the incompletely hydrated phase, if the amount of unreacted C₃S is also known. Unfortunately, the accuracy of this procedure is low because of the low levels of hydration resulting in the determination of residual C₃S. The values of free Ca(OH)₂ content will depend on the method chosen and may, however, also vary with the same cement paste. The C/S molar ratio of the C-S-H phase in the pastes hydrated at room temperature is 1.4–2.0, with a value of 1.7 most appropriate. In some literature [51] the authors do not recognize the connection between the degree of hydration and the Ca/Si ratio. Y. Chen and I. Odler [52] has shown that as the water/solid ratio (w/s) increases, the Ca/Si ratio decreases [53][54].

C-S-H gel can be divided into 4 types according to the structure. Type I is characterized by particles in the form of spines or needles. Type II represents a mesh structure, which arises in the initial stage of hydration, especially in the case of used CaCl_2 additives to OPC. Type III originates in a microstructure where less space to grow particles of this component. Type IV is characterized by particles with a 'perforated' structure that arise in systems characterized by very tiny microspaces with very low ionic mobility. The distinction of types III and IV can cause some difficulties due to the little difference in morphological features [50][55].

Even though the kinetic of OPC hydration is well known, exact composition and structure of C-S-H phase is not fully understood. From the morphological point of view, C-S-H gel can be divided into two types; inner product (Ip) and outer product (Op). Ip forms near the clinker minerals and has higher density, then Op. Ip forms from aggregated globule particles (4–6 nm) and the pore size inside Ip is maximum 10 nm. Conversely, Op has the smaller spatial boundaries, which causes fibrillar structure due to greater access to water. The fibrillar structure is less compact and is characterized by a larger porosity compared to globular (at Ip). The schematic formation of C-S-H phase is shown in fig. 9 [56][58].

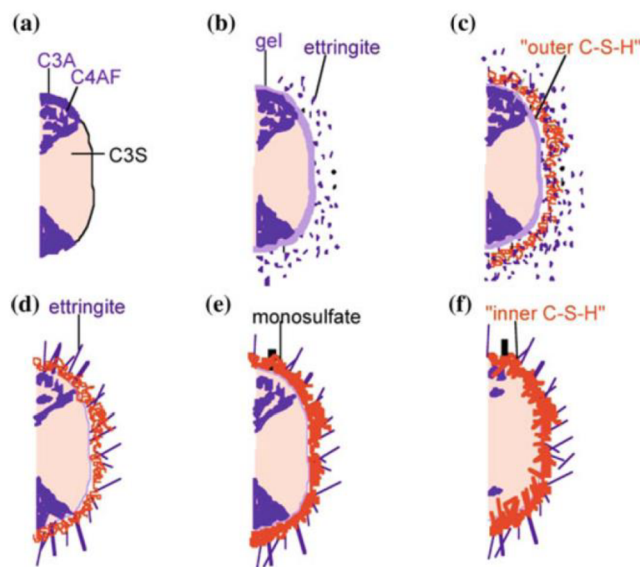


Figure 9 Schematic illustration of anhydrous C_3S phase (a), the effect of hydration after (b) 10 min, (c) 10 hrs., (d) 18 hrs., (e) 1-3 days, (f) 2 weeks [56]

Since the composition of the C-S-H gel is variable, there are certain models that describe its composition based on known minerals. Over thirty crystalline phases of C-S-H are known. Using a variety of sophisticated methods including NMR, XRD, SANS, and TEM it is widely believed to be the analogue of layered minerals, specifically tobermorite and jennite.

Tobermorite

Tobermorite is a natural calcium silicate hydrate, schematic illustration is shown in fig. 10. There are three different types of tobermorite depends on different basal spacing: 14 Å, 11 Å and 9 Å tobermorite. So tobermorite has three different C/S ratio, namely 0.67, 0.83, 1.00 with chemical formulas: $\text{Ca}_4[\text{Si}_6\text{O}_{14}(\text{OH})_4] \cdot 2\text{H}_2\text{O}$, $\text{Ca}_5[\text{Si}_6\text{O}_{16}(\text{OH})_2] \cdot 2\text{H}_2\text{O}$, and $\text{Ca}_6[\text{Si}_6\text{O}_{18}] \cdot 2\text{H}_2\text{O}$ [56].

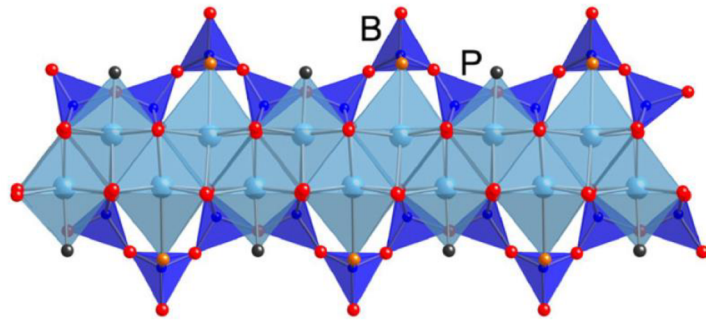


Figure 10 Schematic illustration of C-S-H in tobermorite, regardless of different basal spacing. Schema shows Ca-O layer with silicate tetrahedron attached on both sides, where light blue means Ca, dark blue - silicone, red - oxygen [56]

The most studied type is tobermorite 14 Å, which consist of central layer of Ca-O attached with silicate dreierketten chains on both sides. Ca-O layers are surrounded by water and Ca molecules.

Jennite

Jennite is rare natural mineral which occurring just in several regions on the world: Israel, Germany and Japan. In 2004 Bonaccirsi et al. have been solved a structure of jennite by X-ray diffraction data obtained on a very thin crystal from Fuka, Japan [57]. Crystal structure of jennite is shown in fig. 11. Jennite has chemical formula: $\text{Ca}_9\text{SiO}_6\text{O}_{18}(\text{OH})_6 \cdot 8\text{H}_2\text{O}$. In contrast with tobermorite 14 Å, jennite has greater C/S ratio – 1.5, which corresponds much more to real system of hydrated cement, than any ratio C/S ration in tobermorite [56].

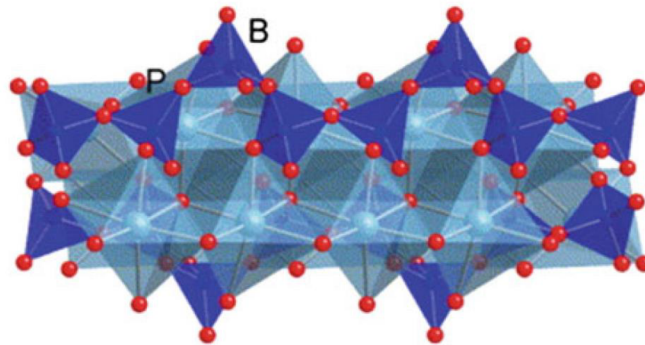


Figure 11 Schematic structure of jennite, light blue - Ca-O, dark blue - silicate, red – oxygen [56]

Many models describing C-S-H structure based on different minerals and different combinations of minerals; however, it is not the aim of this work. Short overview of basic minerals was given for an idea of crystal structure of C-S-H which can be found in real systems [54]. The way how does alkali silicates can influence the C-S-H phase morphology and the whole hydration process is described in the following chapter.

3.4 Effect of alkalis on cement hydration

Alkalis are an integral part of OPC. Alkalis come from raw materials used to produce OPC. It is important to note that the alkalis are mostly in the form of sulfate, a solid solution of silicate or aluminate. Generally, alkalis (in various forms) can influence different types of clinker minerals depending on nature of OPC, pH, rate of hydration, induction periods, etc. The works of various authors are focused on the influence of different alkaline compounds from the

different points of view. Some authors describe the influence of alkali on certain clinker mineral, others characterize the whole hydration running process. Both of these types of work are represented in following paragraphs.

According to the work of I. Odler [59], alkalis, depending on the form of presence (sulphates or doped clinker minerals), can influence the hydration of the cement in various ways. In addition, each alkaline ion does not have to act on the hydration in the same direction. Moreover, I. Odler [59] concluded that the strength development and hydration development of tricalciumsilicate (C_3S) did not change substantially due to the alkalis incorporated into OPC from the raw materials. K_2O accelerates the hydration of C_3A contrary, it slows down when Na_2O is doped. The results of this work pointed out that alkalis accelerate the course of hydration at an early age but suppress later hydration. The addition of alkalis increase the main development of hydration heat with a lower alkali content and reduce the induction period with a high alkali content. The addition of alkalis promote the dissolution of the C_3S phase and the formation of portlandite ($Ca(OH)_2$), but the production of ettringite (AFt) is suppressed. Alkalis adversely affect the compressive strength of cement at the later ages. The compressive strength of cement at the early ages is affected by the alkali content. A negative effect has a high alkali content in the cement, while a low alkali content works positively.

Kumar et al. [60] in their work studied the influence of NaOH and KOH on alite hydration. It is quite clear from the alkali metal hydroxides; they increase the pH of the solutions. In the case of alite hydration, an increase in pH causes acceleration of hydration processes, shortens the induction period, acceleration and deceleration mode. One of the conclusions of this work was that increased alkalinity provided earlier portlandite precipitation and the end of the induction period. Alkaline hydroxides stimulate higher nucleation of the C-S-H gel, presumably due to the higher concentration of silicate [60]. Ma [61] reported that the alkali addition would increase first initial peak (dissolving of the phases) and second heat evolution hydration peak. Previous researchers attributed the accelerating effect to the alkali by increasing the pH of the liquid phase. The solubility of portlandite is inversely proportional to the pH, increasing the pH of the solubility of $Ca(OH)_2$ decreases as well as increasing the rate of nucleation and crystallization of the hydration products [61]. Some authors assume the effect of the alkali content on the formation of the C-S-H gel by; increasing the content of alkali increases the rate of dissolution of silicate and increases the concentration of silicon, which promotes the formation of C-S-H nuclei [62][63]. Juenger and Jennings [64] reported that the initial hydration increased by adding NaOH to the stirring water but slowed down after the first day. Similar results were reached by Bentz [65]. The morphology of C-S-H phase after alkalis adding transforms from a fibre or honeycomb-like to foil-like. In particular, in pure OPC C-S-H fibres grow into isolated clusters, while with the addition of alkali those needles are less developed and do not grow too much from the surface [56].

So far, the effect of alkali on various clinker minerals and the overall course of hydration has been described. Even though cement is a complex system and the addition of alkalis affects not only individual phases of the compound, but also those phases and compounds interact with each other, one could observe the response of the individual molecules to the alkali. For example, Wijnen et al. [66] in their work studied rate of dissolution of amorphous silica gel ($mSiO_2 \cdot nH_2O$) in aqueous solutions of alkaline hydroxide LiOH, NaOH, KOH, RbOH and CsOH. The different solubility of the silica gel in the various hydroxide solutions cannot simply be explained by the difference in the adsorption behaviour of the alkali metal cation onto the silica gel surface. In the range of Cs < Rb < K < Na < Li, the adsorption capacity on the silica gel surface decreases. Obviously, the alkali metal cations must promote the dissolution of silica gel with different encourage. The strength of the propagation effect is influenced by the effective cation radius. In potassium, hydration is impaired when sodium and lithium are heavily hydrated. Sodium and lithium cations are known as water structure constituents, while

potassium, caesium and rubidium cations are known as water structure breakers. This effect is consistent with the degree of solubility of silica gel in alkali hydroxides. Most rapidly, silica gel dissolves in potassium hydroxide than in sodium hydroxide, lithium, rubidium and caesium hydroxide. However, at higher concentrations, the dissolution rates between potassium and sodium or potassium and rubidium are reduced, which means that the differences in the propagation effect of the individual cations are small compared to the overall dissolution rate. Finally dissolving rate increases in order (LiOH~CsOH)<(RbOH~NaOH)<KOH [66].

4 MATERIALS AND METHOD

This chapter is devoted to the description of the raw materials used, sample preparation and instrumental methods used. The first part of the chapter represents characterization of used materials, further part focuses on sample preparation following by description of simple measuring methods. The last one gives information about more sophisticated instrumental methods.

4.1 Materials

This chapter provides information about used materials.

4.1.1 Ordinary Portland Cement

As a primary material for substrate to be treated, preparation the commercial Portland cement, CEM I 42,5 R (HeidelbergCement Group, plant Mokr). Physical and chemical parameters of this cement are shown in tab. 2 [67].

Table 2 List of physical and chemical parameters of used cement [67]

Physical parameters			Chemical parameters			
Parameter	Average value	Standard	Parameter	Average value	Standard	
Compressive strength [MPa]	1 day	16.5	Content [%]	CaO	63.70	
	2 days	30.6		SiO ₂	19.70	
	7 days	50.3		Al ₂ O ₃	4.70	
	28 days	59.7		Fe ₂ O ₃	3.30	
Flexural tensile strength [MPa]	1 day	4.2		MgO	1.40	EN 196-2
	2 days	6.2		SO ₃	3.09	
	7 days	8.1		Cl-	0.06	
	28 days	9.2		K ₂ O	0.73	
Initial setting time [min]	188	EN 196-3		Na ₂ O	0.16	
Final setting time [min]	256	EN 196-3		Na ₂ O equivalent [%]	0.64	
Hydration heat for 7 days [J·g ⁻¹]	310	EN 196-8	Loss on ignition [%]	3.37	EN 196-2	

4.1.2 Alkali silicates

As an impregnation agent were used alkali silicate (WG). A list of alkali silicates used follows in tab. 3, includes production and further adjustment parameters:

Table 3 Alkaline silicate parameters

Parameter	Lithium silicate	Sodium silicate	Potassium silicate
Silicate modulus	3.25	3.38	3.36
Before adjustment			
M ₂ O content [wt. %]*	2.71	7.93	11.60
SiO ₂ content [wt. %]	17.50	25.99	24.81
After adjustment SiO₂ content on 17.5 wt. %			
pH	11.36	11.97	12.08
Density [g·cm ⁻³]	1148	1219	1225

*M in the M₂O equation represents alkalis ion.

M₂O and SiO₂ content were determined by conductimetric titration with HCl; alkalis content was determined by acid-base titration (1M HCl); the SiO₂ by titration after adding relevant hydroxide (sodium water glass – NaOH, potassium water glass – KOH etc.) with continuous conductivity measurement. Density was determined by simple buoyancy method, using densitometers with the appropriate scales, pH was measured by pH meter (SevenCompact™ duo – Mettler Toledo; electrode – InLab^R Expert Pro) and gel point by rheometer Discovery HR-2 from TA Instruments with a geometry consisting of concentric cylinders. More detailed the gel point test will be described in the chapter 4.3.1.

To make the measurement results comparable with each other, the SiO₂ content of all water glasses was adjusted to a value 17.5 wt. % (according to WG) by dilution with water. Adaptation of SiO₂ value to the lithium silicate was from the reason, that lithium silicate is insoluble in water [lithium WG], so it would be impossible under laboratory conditions modify its content.

4.1.3 Colloidal Silica

- Köstrosol[®] 1040
 - SiO₂ content – 40 %;
 - Particle size – 10 nm;

SiO₂ content was adjusted to the value 17.5 wt. % as well as water glasses. All materials from chapters 4.1.2 and 4.1.3 were supplied by SChem a.s. Measured parameters after adjustment of SiO₂ content: pH – 1048, density 1109 g·cm⁻³.

4.1.4 Other materials

Calcium hydroxide

Calcium hydroxide p.a., 95.0 % was used, from the Sigma-Aldrich.

Water

The demineralized water, which was produces at the Faculty of Chemistry.

Aggregates

As a non-reactive component for mortar preparation standard siliceous sand was used according to the EN 196-1 [68]. More precisely, three types of sand of different fractions were used – fine sand (PG I), medium sand (PG II) and coarse sand (PG III). The sand to cement weight ratio in mortars was 3 : 1.

4.2 Sample preparation methods

This chapter describes the methods of sample preparation for various testing. It is important to mark at the outset which samples were analysed. Two sets of samples were tested by each method: the first set (*A*) was subjected to the treatment after 1 hour from the start of mixing, the second set (*B*) after 24 hours.

4.2.1 Paste/mortar preparation

Sample preparation had been done according to the ČSN EN 196-1, using OPC CEM I 42,5 R (HeidelbergCement Group, plant Mokrý). Water to binder ratio in case paste was 0.28 and mortar was 0.4 (determined according to the determination of normal consistency, ČSN EN 196-1 [69]). The whole mixing process took three minutes. Description of preparation steps was as follows:

Paste	Mortar
<ul style="list-style-type: none">○ First of all, weighed amount of water and then cement was placed in a mixing bowl. The countdown began when the cement grains came into contact with water. The first minute was mixed at low speed.	
<ul style="list-style-type: none">○ Stirring had been continuing for the next thirty seconds with increased speed.	<ul style="list-style-type: none">○ A certain amount of standard sand added after the first minute of stirring. Stirring speed was increased for the next thirty seconds.
<ul style="list-style-type: none">○ After minute and a half, the stirring was interrupted, content of mixing bowl had been mixing manually by plastic spatula for thirty seconds.	
<ul style="list-style-type: none">○ Stirring continued at high speeds until a total time of 3 minutes was reached.	

The following sample preparing was depended on using test. Used tests are described in chapters 4.4 and 4.5.

4.3 Silicate characterization

Before direct application of the treatment agents on concrete substrate, the significant step is to understand the behaviour of the pure systems of silicates in terms of their reactivity with the presumed product of hydration of cement.

4.3.1 Gel point measurement

It is important to understand the behaviour of a colloidal system before applying to a cement surface. The behaviour of silicates was evaluated in term of rheological properties, more precisely the gelation time. Alkali metal silicate solutions represent two states, the first being between the dispersion system (sol) and the second transition (gel). The important thing is the transition of the sol to the gel state. From the physical point of view, gel point depends on wide range of factors: silicate modulus, character of silicates (number of monomers, dimers, oligomers) in the colloidal system, dilution rate, ambient temperature, degree of stability. Structure of silicate in the colloidal system is closely related to the age of the system, logically

the older is system is, the bigger probability of the polymer forms of silicate developed. For sure, there several ways how to convert dispersion system into the gel system, the main two types are chemical and the physical ways. In the case of physical gels, these are formed by a change in the physical conditions of the polymer solution, such as a change in pH, the ionic strength of the sol or a change in solvent. If they are chemical gels, then they are formed either by photochemical curing or by a chemical reaction. In the case of reversible gels swelling by adding a dispersion medium to the xerogel. The course of gel formation is significantly influenced by various conditions, the effect of temperature, the effect of concentration and the effect of pH [70].

Due to the fact, that the reaction of silicates with cement substrate (more precisely with portlandite) is accompanied by gel forming, the knowledge of the gel time was crucial. Unfortunately, it is difficult to observe this kind of reaction '*in-situ*', using basic technical equipment, so this reaction was simulated using accessible instrumental facility, specifically rheometer Discovery HR-2 from TA Instruments with a concentric cylinder geometry. To reproduce reaction of silicates with portlandite, 20 mL of the silicate was mixed with the suspension of 0.5 g Ca(OH)₂ and 20 mL distilled water. The moment when the silicate was added to the suspension was define as a zero time. This was followed by manual shaking of the sample for one minute in a test tube. After that, the content of the test tube was poured into the bottom rheometer geometry. After settling the upper geometry in the measuring position, the sample was tempered to 25 °C for another 5 minutes. The parameters of the test were set as follows. The oscillation frequency was 10 rad/s, the amplitude of the strain was 1 %. Storage and loss modulus have been measured in time and the measurement have been running few hours after reached the cross over point. Cross over point means the moment when the colloid system has been converted into to gel state, at this point, there was a significant decrease in the viscous component of the system and an increase in the elastic component. Each silicate had been measured three time and the final result was calculated from the average of these outcomes.

4.4 Basic measurement techniques

This chapter provides information about basic measurement methods, which do not require demanding operators and more complex procedures. These techniques served as a guide for further basic understanding of the behaviour of care agents, before testing them on more demanding instrumentation.

4.4.1 Water penetration test

This chapter provides information about the ability of the film-forming agents to prevent the concrete surface from penetrating water. Two following subchapters describes two kind of used tests.

4.4.1.1 Karsten tube penetration test

Classic Karsten tube is made of glass and consists of a 25 mm diameter circular spout, which ensures the contact of the liquid with the surface to be wetted and the penetration of water or impregnating agent into the mass (fig. 12). The outlet part is followed by an open glass tube with a calibrated scale (4 mL) for measuring the volume of liquid soaked into the material. The tube is attached to the surface of the material to be examined using a fixing sealant and the absorbed amount is read at periodic intervals. The tube and its use have been standardized by several institutions such as RILEM, ASTM and a number of national standardization institutions.

Firstly, necessary to specify, that this test realized on mortar samples. Furthermore, important to describe the sample preparation procedure in advance. Test sample preparation

consisted in filling cylindric moulds (150 mm × 7 mm; diameter × height) with fresh cement mortar directly on the compact table, followed by compaction for 90 seconds. Due to the fact that for the next treatment smoothness of surface is very important, samples surface was smoothed out with trowel. Further moulds were left on laboratory table freely on the air until the surface has been treated. Then both, *set A* and *set B* were treated twice by the appropriate treatment agent by spraying the sealer solution onto the surface.

The time between application was approximately 30 min (depending on water glass/colloidal silica penetration). In addition to treatment agents, samples were treated with demineralized water the same way by the spray gun. The measurement itself took place 24 hours after the agent was applied. Each set were measured at least 3 times. For each sets a reference measurement was performed on an untreated sample. The measurement was realized by the ČSN EN 1925 standard [71], but the time sections have been modified as follows: subtraction from the scale was performed in minutes intervals until 10 minutes, then 2 minutes intervals until 20 minutes and finally in 5 minutes intervals in the rest of the time until 60 minutes.



Figure 12 Karsten testing tube, left for horizontal surfaces, right for vertical surfaces measurement

4.4.1.2 Water absorbability test

According to the procedure of preparation of test specimens based on ČSN EN 196-1, test samples of cement paste in the form of prisms with dimensions of 40 × 40 × 160 mm were prepared. Demoulding of the specimens was realized about 6 hours after the start of mixing. The demoulding was carried out rapidly without expiring 24 hours because of the subsequent treatment was realized the next day and for us it was important the all sides of the specimen to dried evenly. The treatment process was accomplished using various types of reagents (water glass and colloidal silica) by soaking the test specimens in the reagent container for 5 minutes (sample was evenly treated from all sides). After the soaking time elapsed, excess reagent was wiped off with a brush and stored in laboratory conditions, 25 °C, RH ~ 40%, for 24 hours.

The process of water absorption testing (according to the EN 1062-3 standard) itself can be summarized in following four steps:

- i) Weighing samples before soaking into the water.
- ii) Filling suitable containers with water and placing samples in contact with water from all sides.
- iii) At certain time intervals (10 min; 0.5 h; 1 h; 2 h; 3 h; 6 h and 24 h) the sample was removed from the water, wiped with a damp cloth to remove excess surface water and weighed.
- iv) The water absorption was then calculated from the weight changes caused by contact with water, and the results were compared with the reference sample.

Generally, six samples were tested from each type of film-forming water glass and colloidal silica to ensure reproducibility of results and to eliminate possible statistical discrepancies. The individual reference sets were always repeated together with samples of the given series to avoid distortion of the results due to variable laboratory conditions (air humidity, temperature) during the seasons.

4.4.2 Compressive and flexural strength tests

Compressive and flexural strength tests were chosen to assess the influence of the care agent on the strength of the concrete beam. Compressive and flexural strength test is a destruction test according to the ČSN EN 196-1 [69] standard. In our case we used three-point bend arrangement for flexural strength test, then compressive test was done on the two halves of specimens, from the previous measurement. The mechanical properties testing was determined by using the Desttest 4310 Compact A (Beton System, Ltd.).

Testing specimens with the dimension of $40 \times 40 \times 160$ mm were prepared according to the ČSN EN 196-1 standard were after demoulding (24 hours from the start of mixing) treated by sealers the same way as is was described chapter 4.4.1.2, by soaking samples in the container with sealant for five minutes. After 24 hours from the treatment, samples were tested and then in intervals 7 and 28 days. The reference specimens were tested the same day the demoulding was performed and then the next day (on that day, the treated samples were first tested), then in intervals 7 and 28 days.

Generally, five sets of samples had been tested; specimens treated by: sodium, potassium and lithium water glass, colloidal silica and reference. Due to the measurement deviation, from each set there were tested three samples.

4.5 Instrumental techniques

This chapter represents more sophisticated techniques which were used to characterise raw materials and to determine effect of alkali silicate on concrete surface.

4.5.1 Isothermal Calorimetry

The TAM Air microcalorimeter from TA Instruments was used to monitor the changes in the hydration heat generation of the pure cement paste and the paste doped with the treating agents. The principle is to keep the reaction system at a constant temperature. The isothermal eight-channel thermal conductivity calorimeter operates in the milliwatt (mW) range. All eight channels are routed to a single tempered block placed in a temperature-controlled air thermostat. The temperature range of the thermostat is 5–90 °C, with a stability of ± 0.02 °C. The measurement deviation is ± 20 mW with a detection limit of 4 mW.

If heat is released or consumed in the sample ampoule, a temperature gradient occurs on the Seebeck sensor. The temperature gradient produces a voltage, which is then measured. This voltage corresponds to the heat flux at the sensor and the speed of the process in the sample. This signal is continuously recorded in real time.

For each sample, there is a reference that is located on a parallel temperature sensor. During measurement, unwanted temperature influences entering the instrument will have the same effect on the sample and the reference. This arrangement allows very accurate determination of the reaction heat released or consumed by the sample itself, while other thermal processes outside the sample itself are effectively subtracted from the result [72][73].

Measurement was realized in glass ampoules called ‘AdMix’ about the volume 15 mL, which allowed samples and adding agents (water, WG, colloidal silica) tempering on the required temperature, in our case it was 25 °C, moreover agents adding was performed ‘*in-situ*’

and the hydration processes were studied from the beginning. Two grams of cement was always weighted into the ampoule, then the needed amount of water was added, to reach w/c ration 0.5, then in certain period of time, *set A* and *set B*, required amount of agent was added, so that the solution was in contact with the entire surface of the cement, the total measurement time was 60 and 100 hours, respectively. The whole measurement was carried out with constant stirring.

4.5.2 Mercury intrusion porosimeter

To determinate the total porosity and the distribution of the pores of different size mercury intrusion porosimeter was used, Quantachrome Poremaster 33. Besides these two parameters mercury porosimeter allows to determine the skeletal and apparent density, the specific area of the sample etc. The whole measurement takes up a little over an hour and a half. Nonetheless, it is important to recognize that mercury porosimeter has certainly limitations. The main constraint is the fact, that using mercury porosimeter it is possible to determine just the biggest opening pores of the sample. It is important to note, that this technique does not provide information about the actual internal pore size, it only measures the largest pore opening. For obvious reasons it is impossible to measure closed pores, because mercury has no way of entering that pore. With the development with advanced technique, we are able to determine cross-linking structures between pores, due to numerous enumerations. However, that assumptions do not always correspond to the reality.

Mercury porosimeter is a destructive method, after measurement in the pores a significant amount of dangerous mercury remains and during the measurement a pressure of up to 414 MPa is applied to the sample, which can irreversibly destroy the original structure.

The method is based on increasing the pressure of a non-wet intrusion fluid and gradually filling the pores from the largest to the smallest. The instrument operates in two modes:

1) in low pressure mode it begins to fill the evacuated sample and continues through normal pressure up to 3–4 atmospheres (4 μm large pores);

2) then the sample is moved to the high-pressure section where it is measured between atmospheric pressure and maximum pressure of 414 MPa. In current practice, the method is limited from above by pore sizes of about 1 mm, which is due to the high density and hence the hydrostatic pressure of mercury. The smallest detectable pores are 3 nm in size, so this method makes it possible to determine the entire distribution of macro- and mesopores. In addition, the entire measurement typically takes tens of minutes, so this method is so popular despite the potential hazards of working with toxic mercury.

This instrument consists of a low-pressure part at the front right (under the blue cover) and a high-pressure hydraulic chamber at the centre of the instrument with a retractable lid. Under the left blue cover there is a hydraulic oil reservoir and pressure sensors available, the rest of the electronics and the high-pressure transducer are located at the rear. For low-pressure measurement, an external vacuum pump and an inlet of approx. 4 bar nitrogen or dry air are required.

The specimens were prepared of defined size: $7 \times 7 \times 20$ mm from the cement paste into the handmade mould. It is important to maintain the regular shape of the sample so that the instrument can measure the volume of the body. Further the samples were soaked in the appropriate treated agent for 5 minutes in two different intervals: after 1 hour from the start of the stirring (*set A*) and after the 24 hours (*set B*).

4.5.3 Scanning Electron microscopy (SEM)

Scanning electron microscope (SEM) is an important technique, that allows to study the surface phenomena of the material. The main principle of SEM is that the sample is exposed by the high-energy electron beam, that are generated in the cathode and fastened by the affecting

electric field. An arrangement of this technique is illustrated in fig. 13. The result of this interaction of the electron beam with the sample surface is a response in the form of secondary electrons (SE), Augers electrons (AE), backscattered electrons (BSE), characteristic X-ray, breaking X-ray or fluorescence. SEM is useful technique to characterize the material; its morphology, topography, composition, chemistry, crystallographic information, orientation of grains, etc.

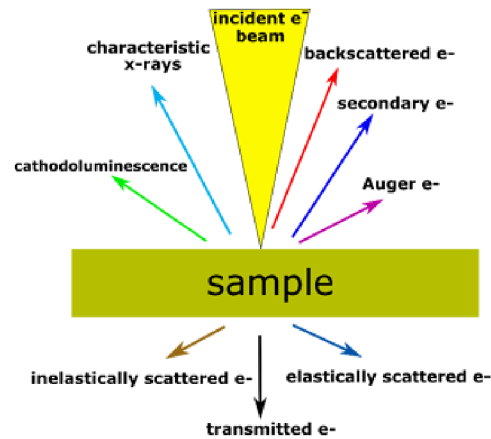


Figure 13 Principle of SEM [74]

Secondary electrons (SE) are electrons that are punched out of the outer electron shells of an atom. The resulting signal is converted to a display unit, and the greater the number of SEs captured, the brighter the displayed point. The SE signal comes from only a few nm. The resolution of SE is 5–15 nm. SE provides sample relief information.

The number of backscattered electrons (BSE) is dependent on the proton number of the element, they are detected by two detectors and the resulting image gives information about the phase composition of the sample. The phase with a higher proton number reflects more electrons and is thus displayed on the screen by a lighter area. The resolution of BSE is 50 – 250 nm.

Auger electrons are the electrons produced when electrons pass from higher energy levels into vacancies, releasing a quantum of energy. This energy can be radiated in the form of a photon (characteristic X-rays) or transmitted to an electron in the outer shell, which thereby gets enough energy to leave the atom and emit an Auger electron. Auger electrons are significantly reflected in lighter elements (C, N, B) and are the basis of Auger electron spectroscopy.

The instrument operates under vacuum and is suitable for solid conductive samples. Non-conductive materials should be coated with metal to prevent sample surface charging. An additional energy-dispersive spectrometer (EDS) measuring characteristic X-rays induced by the interaction of the primary electron beam with the surface of the material is added to the microscope as an additional detection device. Thanks to this analyser we get information about elemental composition.

The samples were prepared the same way as was described in chapter 4.5.2 in the last paragraph, but the dimension was $5 \times 5 \times 2$ mm, due to the geometry of instrumentation. Before soaking by surface treating agents, the surface of the samples was modified by grinding on finer sandpaper to achieve appropriate size, then soaked by the agent for five minutes. The day after treatment procedure (after agent drying up) samples were individually pour into an epoxy resin to eliminate gassing of the SEM measurement cell. The samples surface, the depth of penetration and the distribution of monitored elements were carried out on the JEOL-JSM-7600F microscope. The measurement was performed in the backscattered electron mode.

For obtaining the quality results it is required some form of specimen preparation. The surface should be perfectly clean, free from deformed or amorphous surface layers and, in addition, be flat due to the shading effect. For these purposes standard mechanical or electrical polishing is not enough. The new method was developed based on ion polishing. After the curing of the resin, the side which was analysed was manually smoothed and then polished by ion polishing. Prior to placing the sample in the SEM cell, the surface of each sample was conducted by gold plating. The physical principle of the ion beam polishing technique is described in the following chapter.

4.5.4 Ion beam etching

The ion beam etching (IBE) is a dry plasma etch method, which uses a remote broad beam of ion/plasma as a source, to polish a substrate surface by physical inert gas or chemical reactive gas means. This method is unique due to the large number of advantages among which belongs anisotropy, selectivity, uniformity, wide range of materials are appropriate, precision etch stops, indifferent to substrate shape or thickness, not dangerous to the environment, minimal consideration for health. The substrate is equipped by a pattern mask, but some applications deal with blank. The whole process of the bombardment is well specified and is under control.

The IBE was performed on JEOL IB-09010CP using a neutralized Ar⁺ ion beam of energy $5 \cdot 10^{-16}$ eV, ion density 1 mA cm⁻². A high purity argon was in the ion beam chamber, when the process chamber was held at a pressure of 0.03 Pa [75][76].

4.5.5 X-ray Diffraction analysis (XRD)

Due to the amorphous nature of the treatment substances, X-ray diffraction (XRD) was used only in exceptional cases, more precisely, when after treatment of the cement substrate a crystallized layer (colloidal silica and lithium silicate) appeared on the surface of the sample. In general, XRD is a rapid analytical method that allows to determine the phase structures in the powder material and also to determine the particle size of the sample under investigation. Each crystalline substance is characterized by its unique diffractogram, which is able to identify. This method is based on the constructive interference of monochromatic X-rays with the sample. When X-rays hit the atoms of the studied material, it diffracts and scatters in various directions. Under certain conditions, constructive interference of the diffracted radiation occurs and the direction of the diffracted beam is precisely defined. These conditions are set by Bragg's law.

The primary X-ray beam impacts on the lattice planes at an angle θ and the individual atoms scatter this beam in all directions. In order for scattered (diffracted) interference to be constructive, the path difference of the scattered rays on the individual lattice planes must be equal to an integer multiple of the wavelength of the X-ray radiation used, which is controlled by the *Bragg's equation* (7): [77][78]

$$n \cdot \lambda = 2 \cdot d \cdot \sin \theta. \quad (7)$$

Where, n is positive integer, λ – wavelength of the incident wave, d – lattice plane distance and θ – *Bragg's angle*.

The schematic arrangement of the XRD is shown in fig. 14. In fact, a total of two measurements (characterization of the lithium silicate residue and colloid silicon on the cement surface) were performed using an Emyrean device manufactured by Panalytical. The results were commented in the chapter and diffractograms can be found in the attachments.

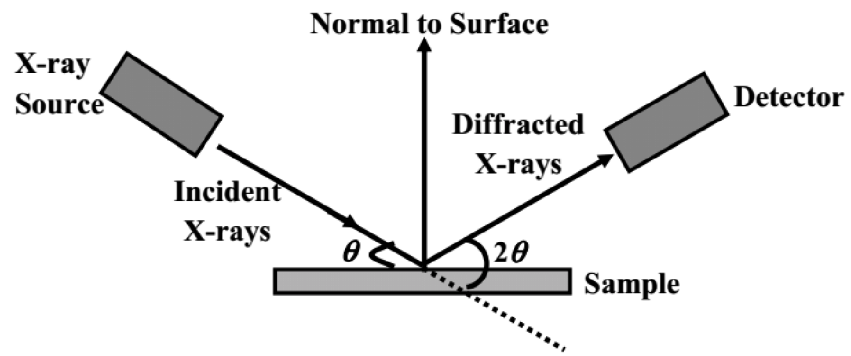


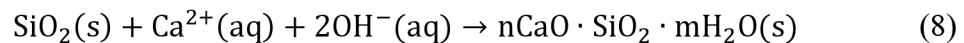
Figure 14 Arrangement of XRD instrumentation [78]

5 RESULTS AND DISCUSSION

This section presents obtained results during the experimental part of the thesis.

5.1 Silicates characterization

Received results are described in ascending order of the gelation time (by the simulating reaction of silicate with portlandite). The fastest gelation occurred in the case of colloidal silica. Essentially gelation took place immediately when the solution of colloidal silica was mixed with the calcium hydroxide suspension. The reason why the gelation happened so fast, that colloidal silica (CS) is actually colloidal solution that formed by dispersion particles of CS in dispersive environment (water), so these particles are not soluble and they played the role of nucleation centres and the gelation runs according to the following equation (8): [47]



The second fastest result was reached by sodium silicate (15.59 minutes), then lithium silicate (20.53 minutes) and the longest gelation lasted for potassium silicate (289.94 minutes). You can observe a graphical representation (dependence on storage and loss modulus on the real time) of the results on following figures: fig. 15–fig. 17. Since in the case of colloidal silica the gelation occurred immediately after mixing the two components, the measurement was not recorded by the instrumental method and the graphical output was also not generated. Determination of the gel point, that is a key parameter, serves as a starting point for evaluating the behaviour of silicate on a cementitious substrate during the next measurements, so results from this test serves as a basis for further measurements.

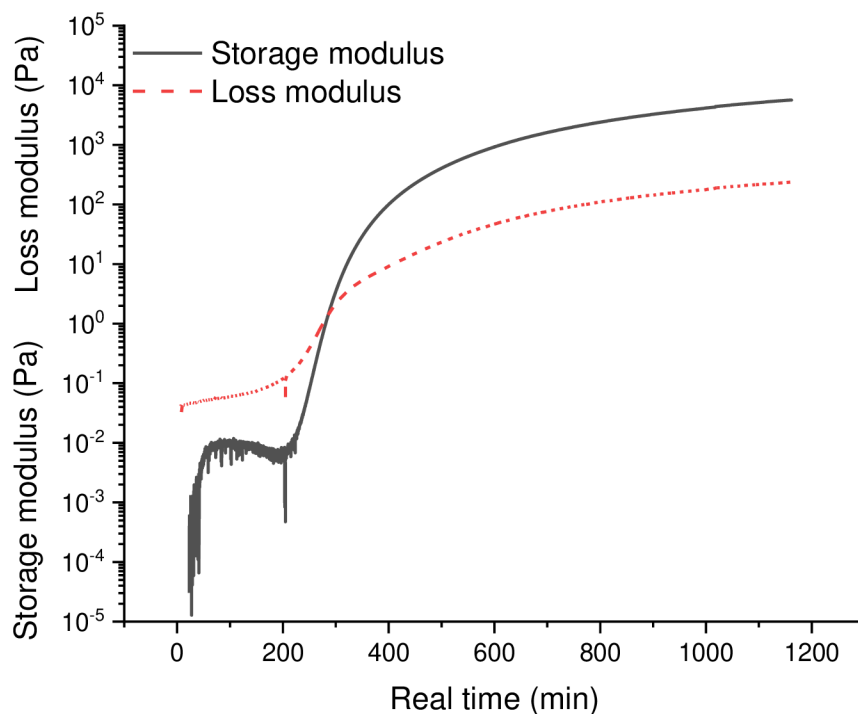


Figure 15 Gel time of potassium WG

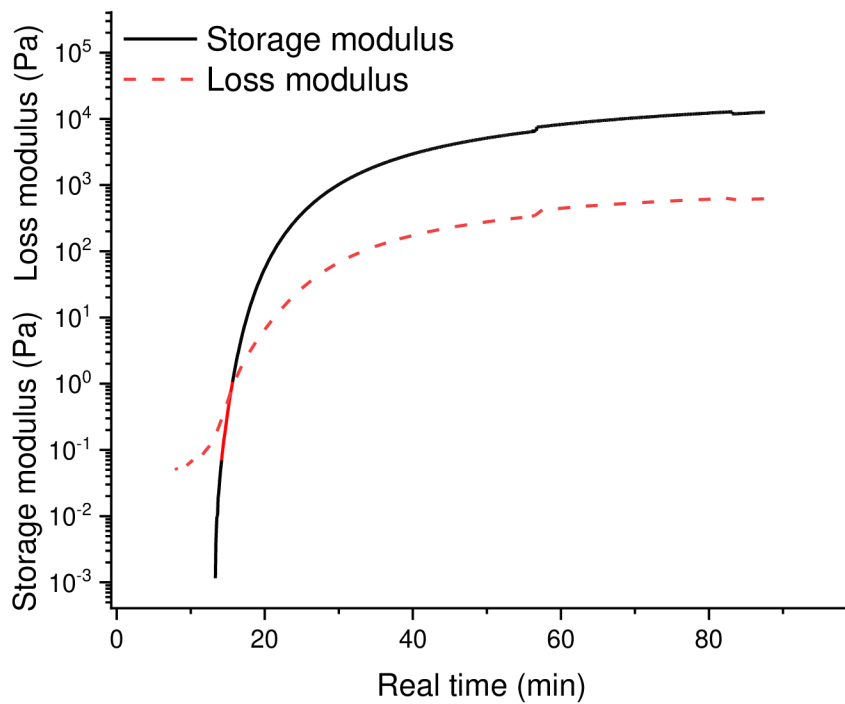


Figure 16 Gel time of sodium WG

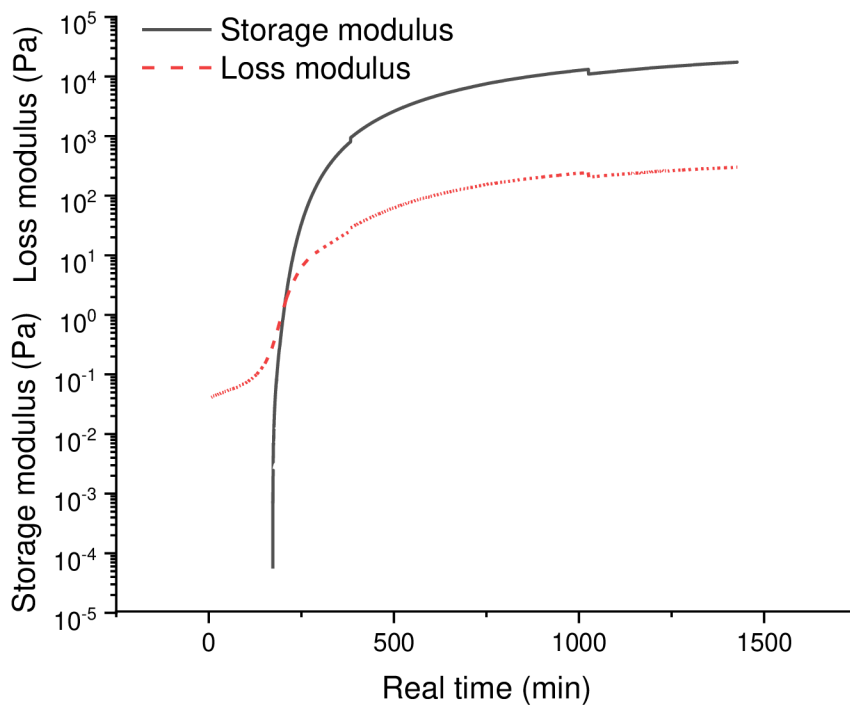


Figure 17 Gel time of lithium WG

5.2 Cement surface response to treatment agents

During the experiments, different responses of the cement substrate to different types of treatment agents were registered. First of all, it is substantive for the goal of this work, that treated samples should have a positive response. Both mechanical and physical changes of treated cement were observed. Exact changes and comparison with reference samples are described in the following chapters.

5.2.1 Influence of alkali and colloidal silica on water penetration

This chapter provides information about degree of resistance samples after treatment process against the water.

5.2.1.1 Karsten tube test

The techniques for assessing the effect of alkalis on water penetration have been selected; Karsten tube test and water absorption test according to the ČSN EN 1925 standard. Firstly, the Karsten tube test will be described.

To begin with, remind, this test was realized on the two sets of samples: the first was treated after 1 hour (*set A*) from the start of the mixing and the second after 24 hours (*set B*). The received results after the both measurements were entirely different. We observed different trends in the behaviour of the treating agents. The same treating substance had almost the opposite demeanour depending on the time of use.

Set A

The results in the set, which we treated after 1 hour from the start of mixing shows interesting trend, but firstly it would be appropriate to discuss about some observation which were noticed after the treatment and which can be related to the received results. After the penetrating of the treatment agents to the cement substrate, it has paid attention to the formed layer on the tested samples. In fig. 18 there are four treated samples, and it is difficult not to notice the white layer on the specimen, which was treated by the lithium silicate, either colloidal silica formed a non-continuous film, but to a less extend. Using the XRD analyse, the content of the films was determined. Lithium silicate caused precipitation of soluble in water lithium carbonate (att. 1) on the top of the samples surface, colloidal silicate in its turn, led to the forming two almost insoluble in water compounds: calcium carbonate, and silicone oxide (is the main compound of the colloidal silica), att. 2. Sodium and potassium silicates formed a continuous, transparent film on the cement surface.

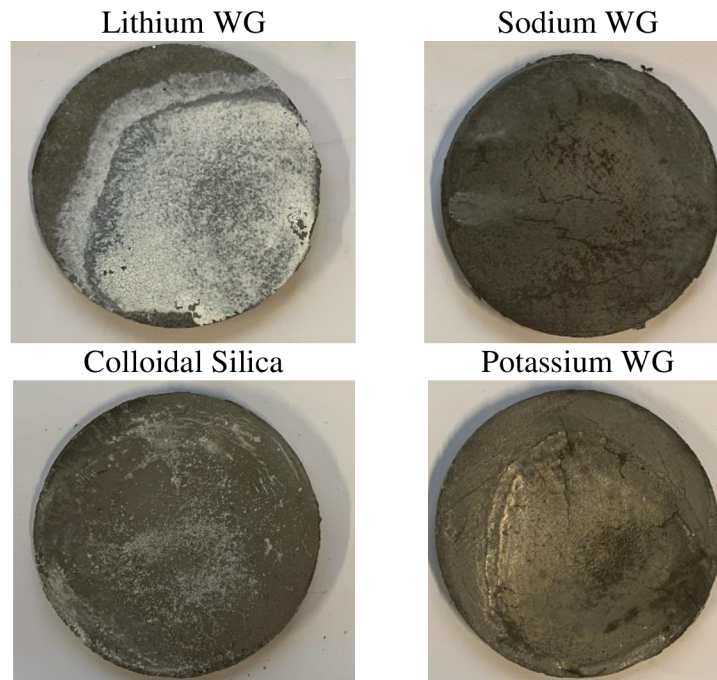


Figure 18 View of the samples after applying treatment agents

Now it is the time to discuss obtained result after Karsten tube test, as the best sample shown up one treated by colloidal silica, with maximum value of absorbability 1.0 mL, then was sample treated just with water (1.3 mL). Values obtained from sodium and potassium WG were quite similar, the reached values were 1.7 and 1.6 mL respectively. The absorbability of referent sample has reached the value 2.1 mL. The behaviour of the next substance was unusual, lithium WG appeared as the worst treating agent with the value 2.7 mL. With the regard to the fact, that application of lithium silicate caused the lithium carbonate (soluble in water), it is possible, that minor part of the 2.7 mL consumed on Li_2CO_3 dissolving and rest of the water penetrated into the cement substrate, so the amount of consumed water is greater that in case of the referent sample. The results are shown in fig. 19.

The reason of this anomalous behaviour can be as a result of incomplete hydration of the cement. It is believed that the alkali silicates, in another words WGs, will get to form a protective layer on the surface and in the pores of the cementitious substrate when it reacts with one of the hydration products – portlandite (CH) [79]. The precipitation of CH from the solution occurs, at the moment of sufficient supersaturation of Ca^{2+} ions and here is also important for us point - the beginning of setting. The initial setting, which was determined according to the standard ČSN EN 196-3, by the Vicat apparatus was 2.5 hours, under laboratory conditions; 25 °C and RH ~ 40%. For us, it means that at 1 hour there is probably insufficient amount of $\text{Ca}(\text{OH})_2$ to carry out the reaction with alkali silicates. In addition to that we can observe the deterioration of the alkali metal WG results in the order of increasing water penetration: potassium WG, sodium WG, lithium WG. Looking additionally into the periodic table of chemical elements, it is found out that trend to correlate with the radius of the molecules.

With the regard to the colloidal silica, according to [45] authors, it shows a pozzolanic reaction that promotes the penetration of SiO_2 particles (10 nm) into the porous cement structure and creates a compact surface structure. It is possible that due to that compact layer colloidal silica formed barrier from water penetration. Probably, the colloidal silica does not require as much CH as it need WGs to start reaction on the mortar surface.

As far as the sample, which was treated just by water, we think, that added water oversaturated the system with moisture, so during the test, the water in Karsten tube had no chance to penetrate the matter which is already saturated.

Set B

With the regard to the second set, which was treated after 24 hours from the mixing, we observe almost opposite trend of compounds behaviour, unlike the first sample set. The deterioration of the results were observed in the series: potassium and sodium WG (0.1 mL), lithium WG (0.8 mL), colloidal silica (1.2 mL) then wetted mortar (1.7 mL) and the last was reference sample (3.3 mL), fig. 20. Regardless to the fact, that lithium silicate led to form the same white crystal matter as it was in *set A* (obviously the same composition), but it did not cause the worst result. In addition, this sequence makes it more logical with respect to the individual properties of the treating agents.

First of all, it would be appropriate to comment WGs trend. We assume that due to the fact, that lithium silicate is basically fine colloid sol, stabilized by Li^+ , so small ions do not heal pores just on the top of the surface, but penetrate deeper into the structure. Obviously, gained values of water penetration between Li WG and Na, K WG do not differ so much, so we suppose that the depth of Li^+ as well as silica ions diffusion can be in tens of microns. Thus, we can assume that lithium WG influences water penetration into the top of the surface to a lesser extent than the sodium and potassium WGs. Difference from lithium WG, sodium and potassium WGs have shown much better resistant to water penetration.

Colloidal silica has shown worse results than lithium WG. At the first glance it would be logical to think that hydration process has been at more advanced stage, so enough CH had been formed and colloidal silica can make pozzolanic reaction with CH and create a compact structure (C-S-H), on the other hand, it can be that the same as lithium silicate, colloidal silica could penetrate deeper into the structure and influence deeper layer because of its nanoparticles. Nevertheless, based on the determination of the gelation point in chapter 4.3.1, it could be assumed that colloidal silica precipitates immediately (by the reaction with portlandite) on the surface of the sample without having to penetrate inside. Confirmation of the deeper penetration of the lithium silicate is discussed in chapter 5.2.5 more detailed.

With the regard to the sample, which was treated by water, we assume, that added water could cause more formation of C-S-H phase, but still it was not enough to reach comparable result which were achieved by alkali silicates. The reference specimen was the most acceptable to the water, because this sample had no protective layer from the moisture.

To compare two sample sets with each other, it can be said, that efficiency of treatment by agents after 24 hours from the start of mixing is better. It results from the fact, that received results from the *set A* are obviously do not respond to the individual properties of the treating agents. Apparently, it is not effective to treat a surface in that short period from the start of the mixing.

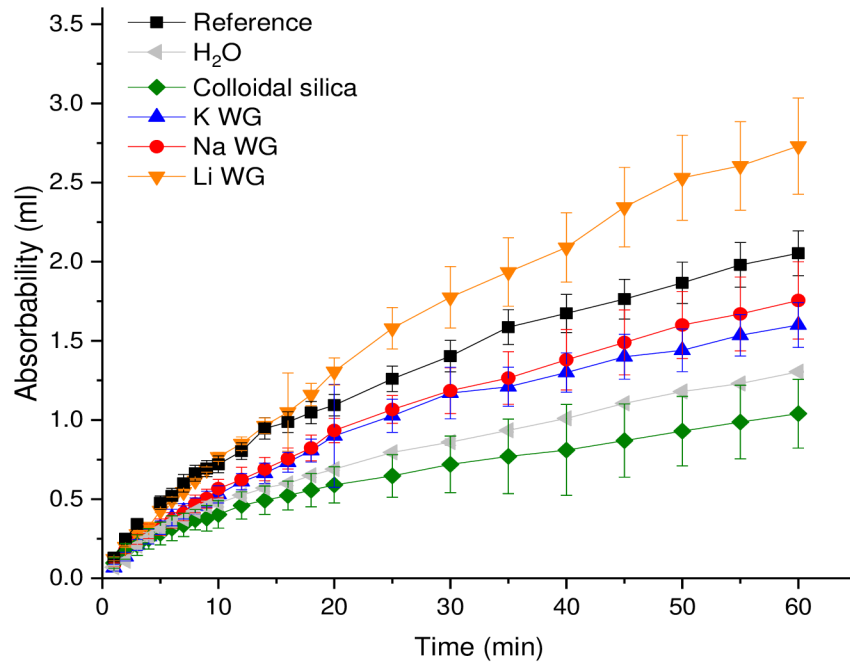


Figure 19 Results of the Karsten tube measurement (treatment 1 hour after mixing)

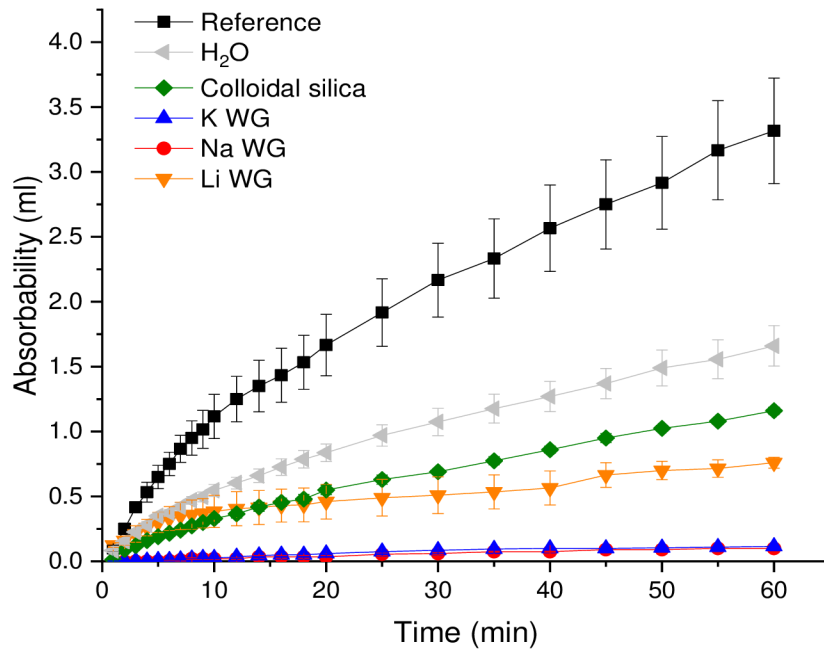


Figure 20 Results of the Karsten tube measurement (treatment 24 hours after mixing)

It would be worth mentioning that this type of test, although standardized, is mostly used for orientation control of water absorbability in industry. This test is influenced by many factors, the degree of sealing of the tube and the surface of the sample, possible negative pressure, and especially in this case open pores in the volume of exudate outside the treated surface.

5.2.1.2 *Water absorbability test*

This absorbability test as well as Karsten tube test, allows to determine water resistance ability of treatment agents on concrete surface. Regardless to the fact, that these methods are very similar, there certain differences between them. Firstly, Karsten tube test is able to analyse only the upper surface of the sample was treated, moreover the test corresponded only 201 mm², whereas in the case of this measurement the samples were treated in the whole volume and the measuring area was 28 800 mm². Due to the possible problems, like seals, surface irregularities, that could occur during the measurement of the Karsten tube, it was risky to set the experiment for a longer time than was chosen, while in this test such problems should not occur instead.

The results from water absorbability test according to the EN 1062-3 standard are shown in fig. 21. To begin with, alkaline silicates (potassium, sodium and lithium water glasses) met expectations and the difference from the reference sample was noticeable. It should be mentioned that the samples were treated after 24 hours from the start of mixing, so that, the main hydration products have been already formed until that time, and silicates, by their nature, were able to form the necessary bonds with the certain hydration products to show their effectiveness. Immediately after 10 minutes, the efficiency of the silicates was manifested, their absorbency was approximately 3.5 times lower than the reference (note, the water absorption was measured by weight gain of samples). Silicates maintained this trend throughout the whole testing period (24 hours), with respect to the measurement deviations. The differences in values among the alkali silicates correspond to the standard deviations, so that these results can be considered as equivalent.

Next on the list of substances is colloidal silica (CS), which obviously had certain difficulties on the way to achieving good results, therefore it appeared as the worst treatment agent. After the colloidal silica drying, the white cracked film was observed on the specimen surface, which had no adhesion to the concrete surface. Here, it would be appropriate to refer to the chapter 5.1, where it was found, that gelation of colloidal silica and portlandite occurs immediately. So, it can be assumed, that interaction of CS with concrete surface was followed by the gel forming, without deeper penetration of the treatment agent.

The treatment with water is more likely to contribute to oversaturate the system. Surplus water has no chance to evaporate or used up during the hydration process (until the measurement have started), so this samples are wetter that others and it is obvious, that oversaturated system is not able to adsorb more water.

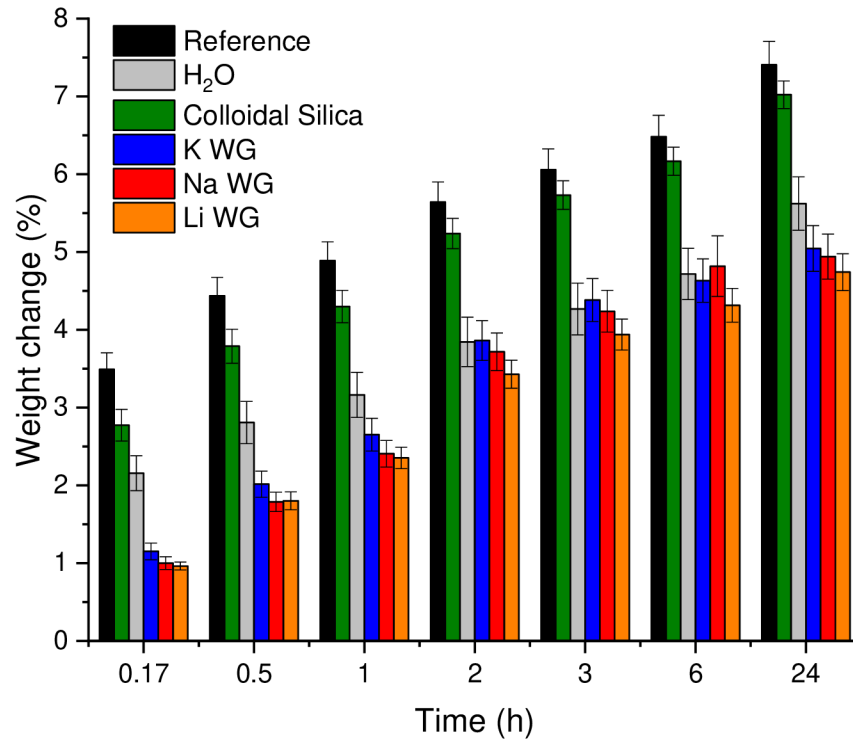


Figure 21 Results from the water absorbability test according to the EN 1062-3 standard.

Comparing two methods mentioned above, it can be said that the results of *set B* from Karsten measurement and absorbency according to the EN 1062-3 standard correlate with each other. It can be seen that water glasses contribute to the reduction of water permeability.

5.2.2 Influence of alkali and colloidal silica on the mechanical properties

The treatment compounds were expected to cause pore closure so that all the water inside the samples does not evaporate, thereby providing a higher degree of hydration and, as a result, more amount of binder phase (C-S-H gel) is created and thus higher material strength could be observed. Unfortunately, in fact, the obtained results did not bring our expectations. We have to submit, that the difference among treated samples is minimal and we cannot to claim that treatment agents improve mechanical properties during the first 28 days with respect to the error bars (fig. 22 and fig. 23)

Researchers have been still discussing the negative effect of alkali content in cement on the mechanical properties at later ages [85], for example Osbaeck [80] and Jawed and Skalny [81] in their works reached the similar results, which are consist in the conclusion, that the high content of alkalis increase the compressive strength in the early age, but then follows by the decline of the strength after the 28 days.

However, what about effect of alkalis in the cement in early ages, there are some positive discussions. Sant [82] published that in the early ages, the system saturated by alkalis reports better compressive strength during the first day, but further the plain (reference) system showed higher strength. Nevertheless, in our case, we did not observe significant differences among the reference system and treated samples by alkali silicates and colloidal silica in the early ages, it could be by the reason that our system did not saturated of alkali silicate in the full volume. Contrary, the publication by Smaoui [83] has not been confirmed, that alkali addition affects the compressive strength during the hydration process. In our case, we have not seen such a big

difference between specimens either, those differences were rather within the measurement deviation. As Odler [55] reported, the small amount of alkalis has a positive effect on the compressive strength, nevertheless oversaturated systems show the opposite effect. Odler and Wonnemann [84] observed, that incorporated alkalis in the cement clinker had no influence on the compressive strength, however the adding alkalis substantially reduce the strength any age up to 28 days.

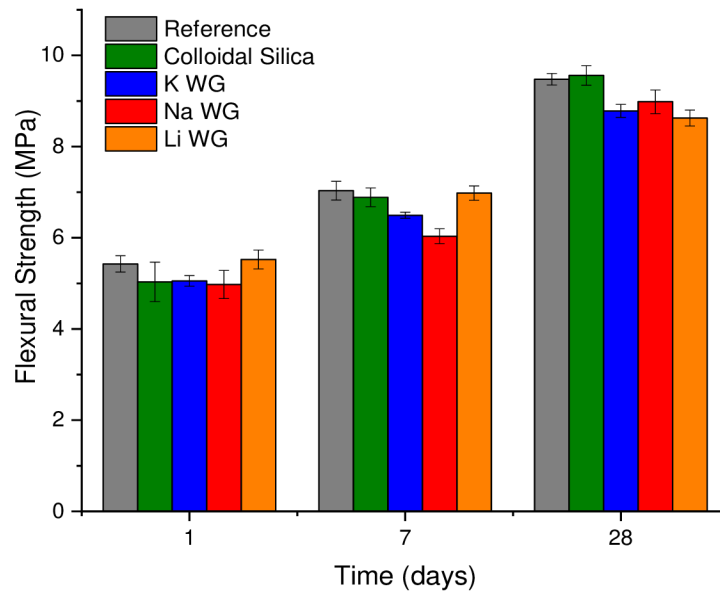


Figure 22 Flexural strength dependence on time

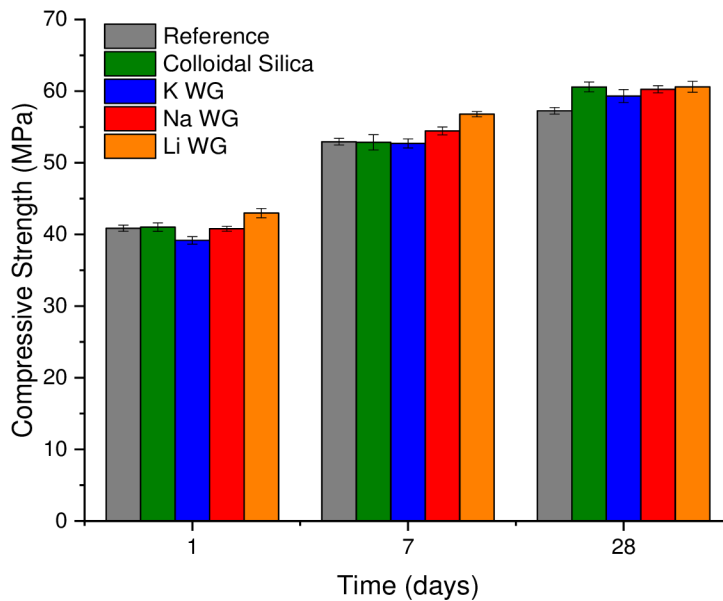


Figure 23 Compressive strength dependence on time

So, as a partial conclusion, we can conclude, that treatment by alkaline silicates and colloidal silica did not bring significant different against the reference specimen, observing deviations from the pure system were in the limit of error bars.

5.2.3 Calorimetry measurement

This measurement provided us the information about effect of alkalis and colloidal silica on the cement hydration. Hydration of OPC (without additives) is characterized by two main peaks: first initial peak corresponds to the dissolving of the silicate phases (duration about 10 minutes), second is the main hydration peak, another words – ‘silicate peak’, is associated with hydration of C_3S and connected with the formation of the second-stage C-S-H phase and the precipitation of portlandite (CH).

Due to the treatment during the hydration process “*in situ*”, we can observe the new peak related to the admixture additions (marking of this peak for the better clarity will be 'alkaline peak'). The first initial peak (which corresponds to the phases dissolving) has the same meaning in both cases, it generated due to wetting and hydration of clinker phases. The first initial peak is the only the same part in the calorimetric curves of two different sets. So, the new ‘alkaline peaks’ appeared either closely after the first initial peak (*set A*), or after the main hydration peak (*set B*), depends on the treatment time.

To summarize, in both sets we obtained **3 hydration peaks**: first initial peak, the main (‘silicate’) peak and the ‘alkaline peak’.

Set A

In general, treatment after 1 hour considerably influenced hydration flow. As you can see in Figure 24, ‘alkaline peaks’ (peaks marked with ‘*’) belong to the moment when alkalis and colloidal silica were added. These peaks respond to the reaction between $(SiO_4)^{4-}$ and Ca^{2+} to form a gel like C-S-H [86].

The beginning of induction period of OPC without any add of treatment agents was determined on 0.88 h, so it is very close to the moment, when additives were added. In induction period the pH of the solution slowly increases due to the slow dissolution phase, and the solution begins to saturate with Ca^{2+} ions, so the WG immediately reacts with these cations and this is the reason why the reaction between WG and cement paste run very fast. In addition to that the amount of additive was very little (0.1 mL, this amount was calculated just to cover the top of the cement paste in testing ampoule). Due to the small amount of formed Ca^{2+} in this moment, when the additive had been dosed, Ca^{2+} ions were immediately depleted for binding and form little amount of the new hydration product. It is assuming, that additives would build in the structure of the calcium silicate hydrate and modify the morphology of the C-S-H gel.

Different amount of hydration products has been formed depending on the additive. The amount of hydration products corresponding to different types of water glasses and colloidal silica has been calculated by integration of the area under the peak.

According to the contribution to the development of heat of hydration, the used treatment agents could be sorted as follows (in descending order): sodium WG > potassium WG > lithium WG > colloidal silica. In terms of the formation of hydration products, the effectiveness increased as follows: sodium WG > lithium WG > potassium WG > colloidal silica. The results are shown in fig. 24. in the enlarged part of the diagram.

Now it would be appropriate to discuss an influence of the alkali silicate and colloidal silica on the ‘silicate peak’, which corresponds to the main hydration stage. The development of this peak is slightly influence by WGs and colloidal silica presence in the mixtures. Generally, additives have caused the shift of this peak to the later time and led to mitigation of the early

unmentioned peak which correspond to the depletion of sulphates (this peak is not crucial for this experiment, so will not be described further).

When compared with the reference sample, the least influence on the ‘silicate peak’ had colloidal silica. From the above values can be concluded that we can see a following sequence. Sodium WG causes the highest maximum of the ‘silicate peak’ and leads to the biggest shift to the later time of the silicate peak. The other extreme is behaviour of colloidal silica, which least affects the ‘silicate peak’ and causes the main C-S-H forming in shorter time. Overall, we can say that the greater the development of the heat flow water glass causes during the second hydration peak (corresponds to the agent adding), the bigger shift to the later time of the ‘silicate peak’ displays. Our results are in agreement with Bentz’s [65] work and correspond to the fact that the alkalis present in the used water glasses accelerate the hydration process of the OPC in the early ages but reduce the degree of hydration in later age.

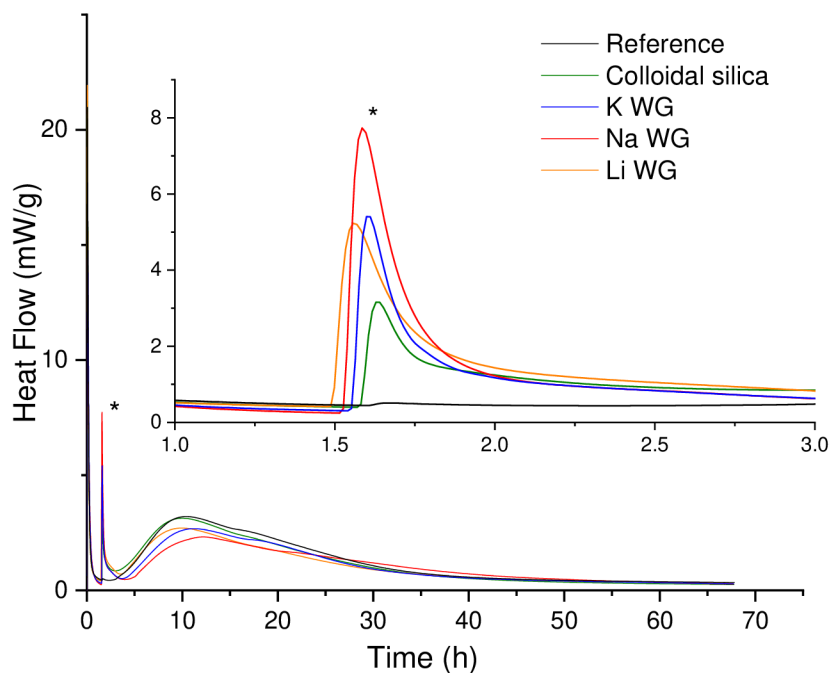


Figure 24 Heat flow development in time after treatment (1 hour)

From the calorimetric curve which illustrated the heat flow of hydration in time was determined the hydration heat flow, then maxims of the peaks and areas under the peaks were calculated to find out the developed heat and the amount of hydration products. The total relaxed amount of the heat was determined from the curve of the heat in time fig. 25.

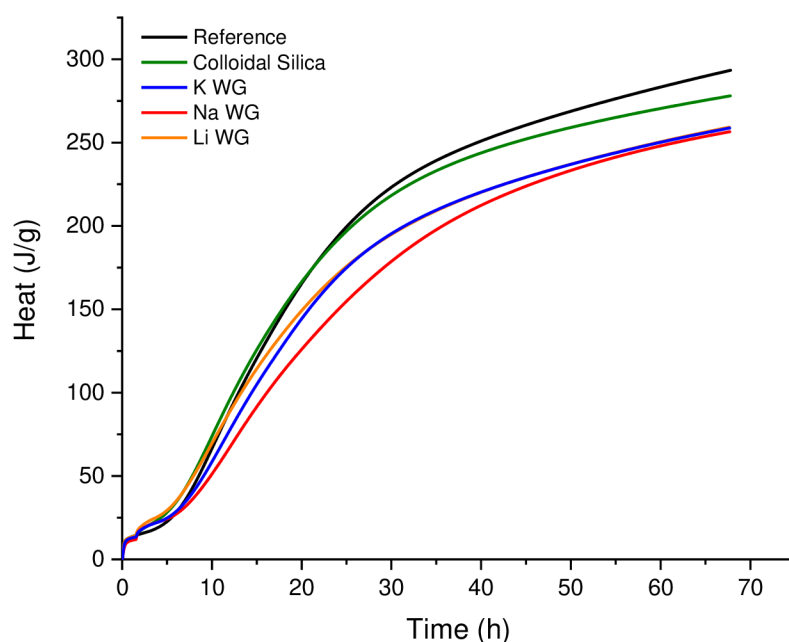


Figure 25 Heat production in time (1 hour)

Set B:

The same as in the *set A*, the hydration curve had 3 characteristic peaks: the first initial, ‘silicate’ and the ‘alkaline peak’ responds to the added treatment agent. The trend in reaching the maximum and minimum heat flow is the same as in the first series of samples. According to the intensity of the development of hydration heat at the moment of adding the treatment agent, the used compounds can be sorted as follows (in descending order): sodium WG > potassium WG > lithium WG > colloidal silica. To compare with values of maximum with previous set, it is obvious, that current values have lower maximum. We assume that the reason why we achieved lower values is, that after 24 hours the cement in the ampoule is already set and the cement paste is in the phase of hardening, so the treatment agent reacted just with the surface, not with the whole volume of the mixture (how it was in case of treatment after 1 hour, after 1 hour mixture was still liquid and adding agents had chance to react with the whole volume of the mixture). Due to the fact that by the time 24 hours from the beginning of the mixing, the main hydration processes have been in the more advance stage and the most part of the main hydration product like C-S-H gel and the second abundant product portlandite have been already formed, that is, the treatment agent has no other choice but to react with the already created CH to form C-S-H phase [85].

The amount of product formed is approximately the same as that produced in the first series of samples (evaluation was performed from the area under the peak). By the reason that after 24 hours there was enough precipitated portlandite, the reaction between WG and CH is more effective which is manifested by a sharp intense peak fig. 26 and then only after all the bonds have been formed hydration continues.

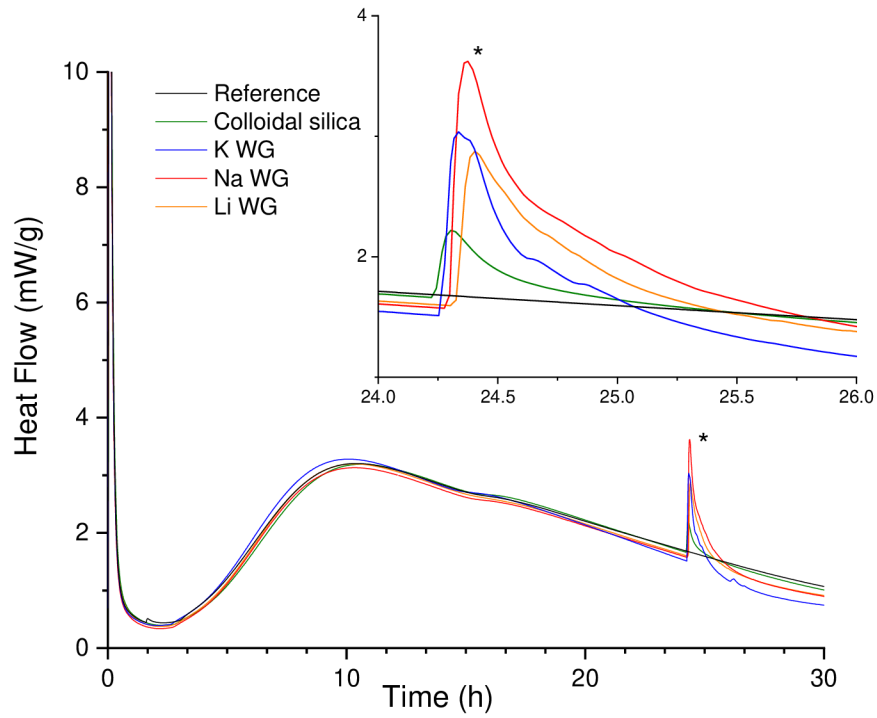


Figure 26 Heat flow development in time after treatment (24 hours)

The general hydration heat of cement hydration until 60 hours has the same regularity as in the first set and decrease in the line (fig. 27): reference > colloidal silica > lithium WG > potassium WG > sodium WG. This trend based on the same principle which was discussed in *set A* and which had proof by Bentz's [65] conclusion, that have been already mentioned.

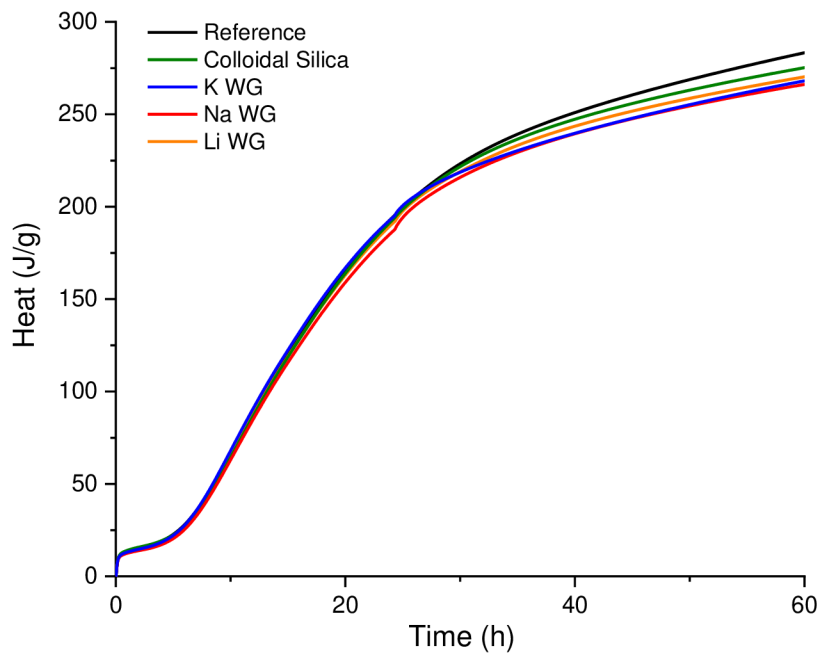


Figure 27 Heat production in time (24 hours)

A partial conclusion of this measurement can be made on the basis of two sets, the addition of alkali really influences the course of hydration, so that accelerate its course in the early stage. The more heat is generated during the addition of the treatment agent; the less total hydration heat is generated. As the pH increases with the addition of alkali, the solubility of $\text{Ca}(\text{OH})_2$ decreases, which means that the concentration of $\text{Ca}(\text{OH})_2$ increases. Consistent with Kumar's [60] findings, increasing the pH (via addition of alkali) accelerates hydration.

5.2.4 Porosimeter measurement

The aim of this measurement was to verify, how does different types of WG and colloidal silica are able to heal open pores. Because inorganic materials like water glasses are considered as pore blocker, which have partial or total pore-filling effect and thus reduce the surface porosity. [88]

The plot of the porosity in ‘%’ (i.e. the percentage of the total sample volume) on the pore size distribution was demonstrated. The beginning of the axis X was chosen to correspond to the minimum value that the Quantachrome Poremaster 33 machine is able to detect. It is important to mention, that the reference sample was measured in both series, thus eliminating the measurement error. The results of the reference sample were almost the same in both cases, which allowed us to compare the series with each other and especially to compare the treated sample with the untreated sample.

Set A:

The results from the *set A* (fig. 28), which was analysed after the treatment 1 hour from the start of mixing cannot be unequivocally to comment, because there is no any regular trend in behaviour based on the chemical and physical properties of individual treatment agents. It is assumed that it is caused by the reason, that 1 hour it is too early for the system to form compact porous system. This time it is still a heterogeneous solution of water and cement, even if the sample is held together. Since the water glass is in water solution and a large proportion of this solution has water (as was determined by conductometric titration), one consider that the water glass contributes more to the hydration of cement. As it was detected by the calorimetric measurement chapter 5.2.3 at the moment of adding water glass to the cement/water system hydration peak appears which is arguably correspond to the reaction of water glass with Ca^{2+} ions and form something like C-S-H gel [86]. Thus, the water glass in this case serves as a support for the formation of cementitious structure but does not fill pores with new hydration products.

Set B:

Greater rationality was provided by samples that have been treated 24 hours from the start of mixing, *set B* (fig. 29). The second sample series gives a broader field for discussion. It be can submitted, that inorganic surface treatment almost eliminated pores larger than $0.655 \mu\text{m}$. From the point of view, the effectiveness of individual represents of water glasses can be ranked with decreasing efficacy into a series: potassium WG > sodium WG > and lithium WG. It was not unequivocally clear, but it seems that the sequence corresponds the cation radius, the bigger radius means higher efficiency of the pore healing.

In addition, it is important to remind, that both sets were measured 48 hours after the mixing. Based on this information, we can observe that samples, which was treated after an hour from the stirring have the similar running, pore content and pore sizes as the reference samples from the both sets. So, it could be the proof, that adding of WG after an hour leads to formation of same porous system as the porous system without adding, so WG cannot be a pore filler in the first set. Nevertheless, it cannot be arguing, that there is a direct dependence of the radius of the ion on its healing ability.

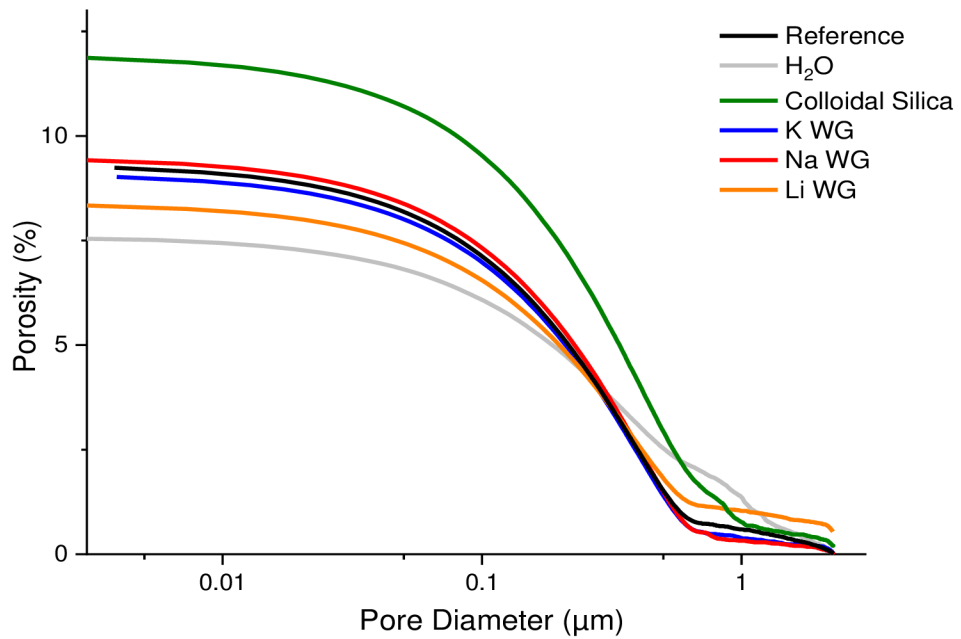


Figure 28 Effect of treatment agents on porosity (treatment after 1 hour)

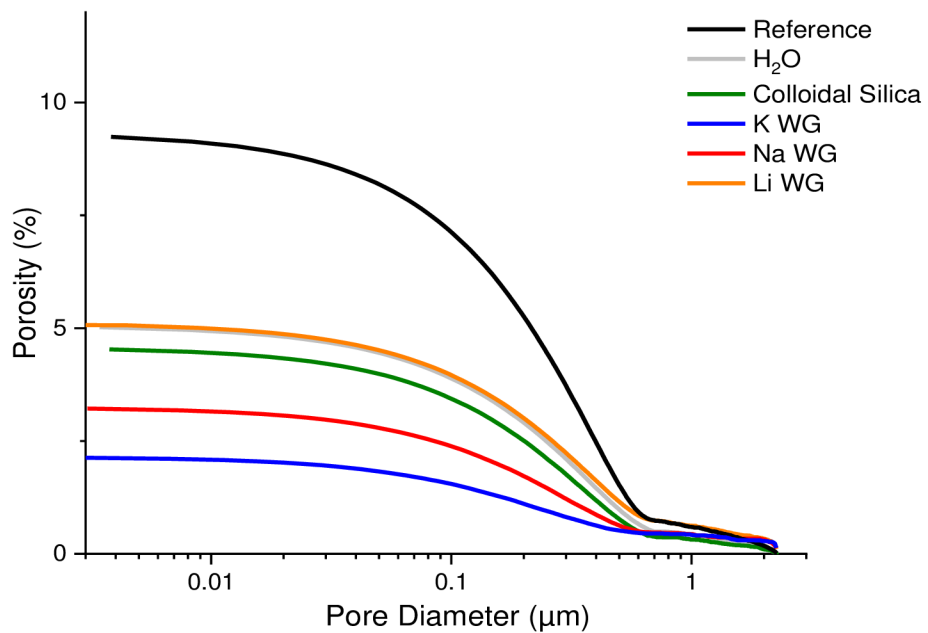


Figure 29 Effect of treatment agents on porosity (treatment after 24 hours)

It would be appropriate to compare the results from the measurement of porosimeter with the results of water absorption according to the EN 1062-3 standard (in chapter 5.2.1.2), because pore healing of the cement surface results in a reduction of water permeability. A significant decrease in porosity can be seen in the treated samples, which is also confirmed by the lower degree of absorbency compared to the untreated sample.

5.2.5 *Microstructure of concrete surface*

SEM images showed the character of the film-forming layer, which is very visible on the surface of the cement substrate. In all cases the following parameters were evaluated: penetration depth of the treatment agent, distribution of the certain element (alkalis, calcium and silicon). The investigated layer was about 100 μm . In the following paragraphs, individual effects of silicates on the concrete surface will be described. Chemical elemental mapping revealed the distribution of individual elements both in the layer and in the hydrated cement paste.

Sodium silicate

Let start with sodium silicate, because this type of water glass is the most wide used in the field of surface treatments. In fig. 30 you can see an image from the SEM-EDS of the sample, which was treated by sodium WG, the treated surface is on the bottom part of the figure. The high concentration of the silicone on the top of the surface seems to be remarkable, notwithstanding that there is no presence of calcium, so it can be assumed, that on the top of the surface there is no C-S-H gel formed (if it were a C-S-H gel, calcium would also be present). The presence of the silicon on the top of the surface is clearly visible, but above that it was verified by the creating the point spectrum, corresponding to 'Spectrum 13', which provided us an information about elemental composition and only silicone and oxygen were there in the largest predominance over the minority elements. It is likely to be a kind of silicate, that was formed due to water glass drying, but this layer does not form any chemical barrier because it does not form any bond with the cement surface.

Then, depth of the sodium penetration can be pay attention; one can estimate approximately 30 μm (with respect to the scale). Penetration can cause the start of ion exchange reaction, where Na ions replace Ca ions to form C-S-H gel with lower ratio of Ca/Si how do Jiang, Lihong et al. represents in their work [13]. The same as Hou et al. [46] perform in their work.

Next, the large number of the cracks cannot be overlooked, origination of the cracks cannot be certainly determined, whether they formed during mechanical grinding of the sample before applying the care agent, or formed during ion polishing, because the device works under high vacuum and water, occupied both water glass and in the sample itself, can expand due to the vacuum and can cause shrinkage cracking. From the Si and Na elemental mapping images shown in fig. 31 and fig. 32 it can be seen, that obvious inner 'pores' exist in Si ion mapping image, whose positions fit with 'Na clusters' in Na ion mapping image very well. So, we can expect, that Na ions fill the inner pores and created a bond with the hydration products of the cement substrate. In some part of the samples surface we can detect places in Si ion mapping image with outer cracking rips, which are in Na ion mapping image are stored by a kind of sodium compound which seem to be different from the inner one (because of response and intensity). With the respect to the fact, that samples were undergo treatment procedure in oxidative atmosphere (air), addition to that the amount of the treatment agent was in surplus, we can suppose, that the excess amount of sodium silicate filled the outer cracks and carbonated (by the CO_2 present in the air) to form of sodium carbonate.

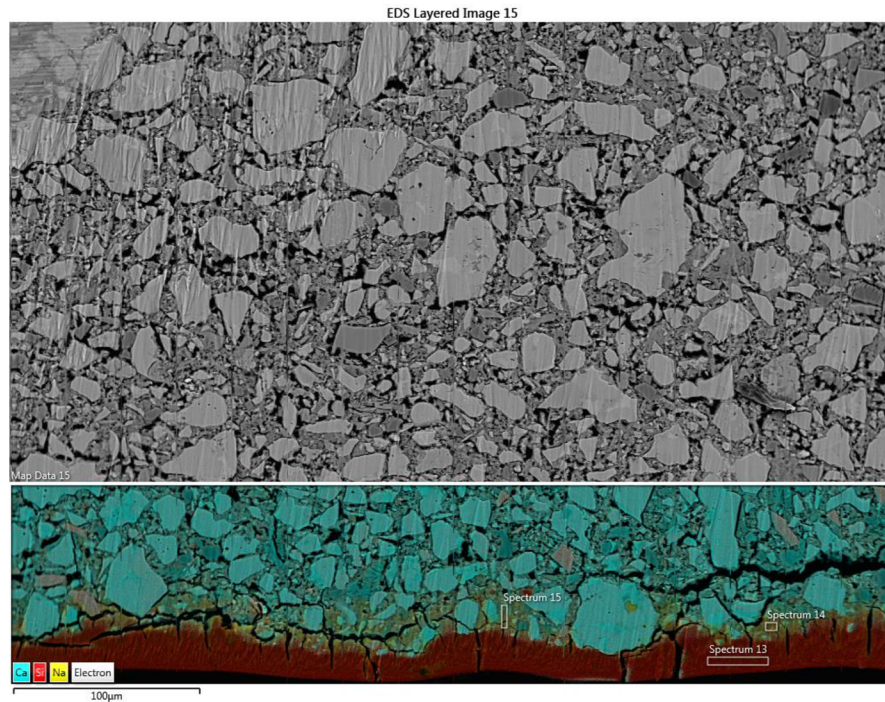


Figure 30 Overall element map of the sample, that was cured by sodium WG

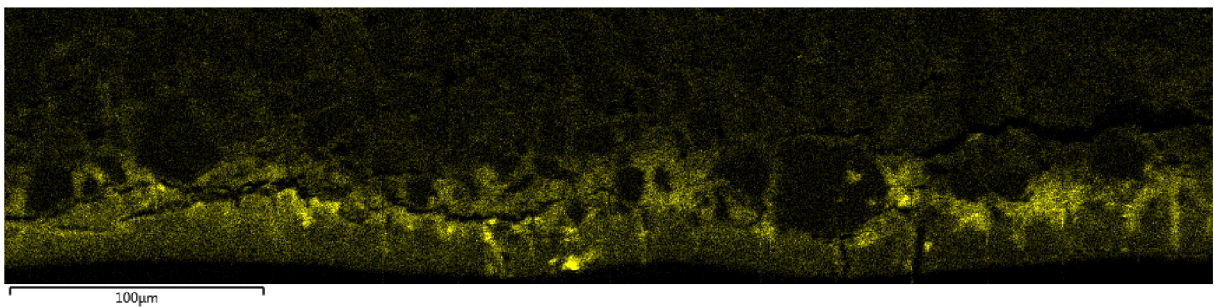


Figure 31 Sodium element map

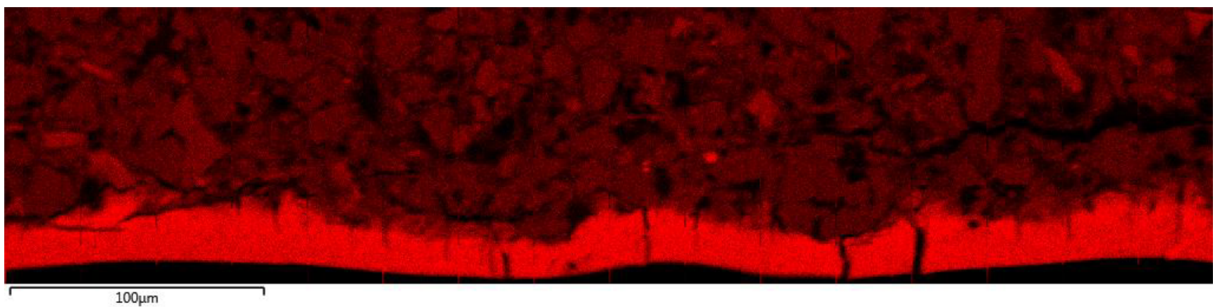


Figure 32 Silicon element map (sodium WG)

Potassium silicate

Let us continue with influence of potassium silicate on the microstructure of the cement paste. In contrast with sodium silicate, potassium silicate is not as deeply studied as sodium, so mechanism of the interaction with cement substrate can be much more unclear. However, based on the images from the SEM-EDS analyse, we can presuppose the behaviour, and degree of interaction of the potassium silicate with the cement surface.

First of all, it would be correct to start with overview elemental map, which is shown in fig. 33 (treated surface is on the bottom of the image). Even potassium water glass could not

eliminate the number of cracks, the origin of which is not unambiguous, they could be caused by mechanical treatment of the sample or vacuum of instrumental techniques.

On the contrary with the sodium silicate, the interaction with cement substrate in thinner layer can be estimated, approximately about 10 μm . So, it could be supposed, that the potassium silicate does not penetrate as deeply as sodium. The reason of the less penetration could be a bigger ion diameter, which prevents deeper infiltration. The degree of crosslinking of the potassium silicate solution (this is affected by the age of the system) can either makes sense regarding to the penetration.

Continuous layer on the top of the specimen is likely to be residual water glass, which probably hardened due to drying and may does not affect the internal microstructure of the cement substrate. Based on knowledges about mechanism of interaction sodium silicate with cement substrate, one assume the similar essence, which means, that alkali silicate has to replace Ca ions to modify C-S-H phase and create a chemical bond with cement substrate. In fig. 34–36 can be a proof of the fact, that the top of the surface is really residual potassium water glass, because there are no calcium ions there.

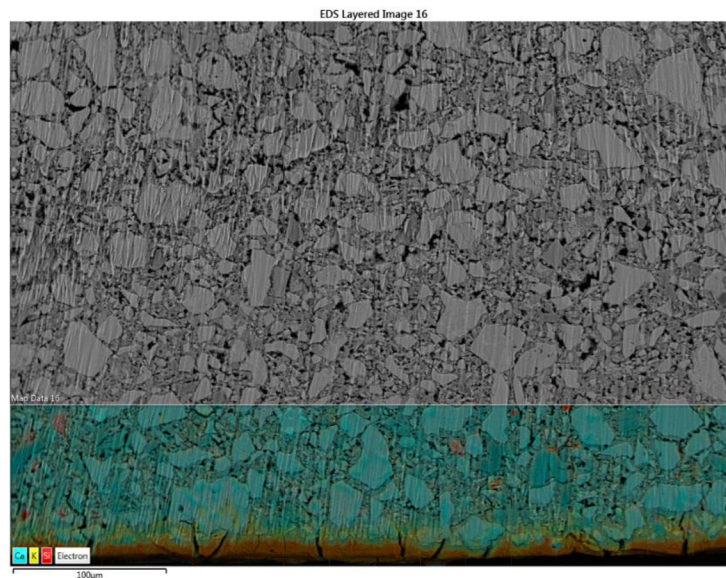


Figure 33 The overall element map of the specimen cured by potassium silicate

Nevertheless, in some deeper parts of the sample the new phase, where water glass was probably interacted with the cement substrate and the change of the microstructure were observed in fig. 34 and fig. 35 (marked areas 1' and 2'). In that places K ions are likely to replace Ca ions and react with cement hydration products, but, unfortunately, there are not too many parts where it is possible to observe this kind of substitutes, and one cannot claim that there would be a drastic change in the structure that would affect other properties of the cement substrate. Fig. 36 illustrate a distribution of Si.

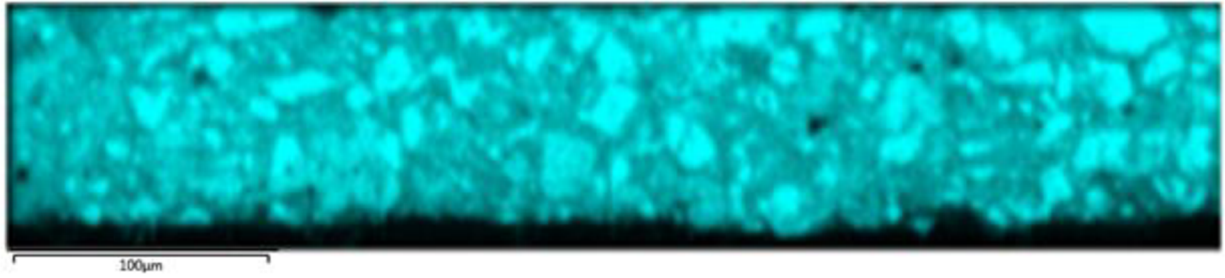


Figure 34 Calcium element map

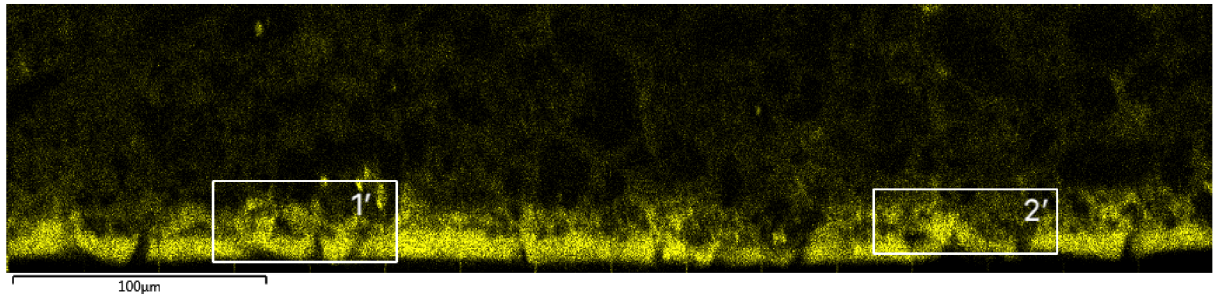


Figure 35 Potassium element map

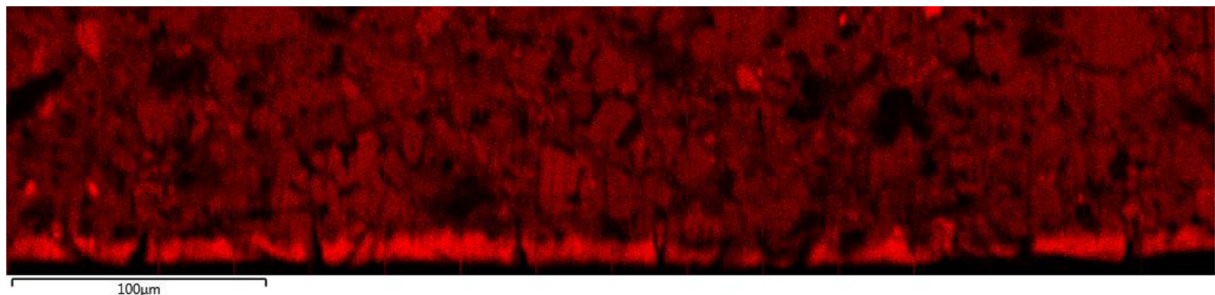


Figure 36 Silicon element map (potassium WG)

Lithium silicate

To begin with, it is important to explain, that instrumentation of SEM-EDS has certain limits and do not allow to detect elements which mass is lower that beryllium and unfortunately lithium belong among the element that are out of detection limits. So, unfortunately it is impossible to estimate a rate of penetration and the distribution of lithium. Nevertheless, it is possible to gauge the distribution of lithium due to the places where Ca and Si ions would occur together and are likely to create a phase corresponding to the composition of the C-S-H gel (the penetration of Si ions into the cement substrate can be monitored). The reason why it is conceivable way how to reveal the Li ions, that lithium silicate besides the lithium ions contains a large shape of silicate ions.

As it is shown in fig. 37, in addition to the dense concentration of Si ion on the surface of the sample (corresponding to residual water glass), there is a certain distribution in the greater depth of the sample, but the large grains, corresponding to Si ions, have nothing to do with the continuous phase. these are probably sand grains that got into the sample during processing in the laboratory. Deeper distribution of Si is estimated to about 50 µm, where the network of Si among Ca ions is observed. It can mean, that lithium (due to small ion diameter) allows the water glass solution to penetrate deeper and influent rather deeper layer, not the top of the cement surface. That penetration causes the start of ion exchange reaction, where Li ions replace Ca ions to form C-S-H gel.

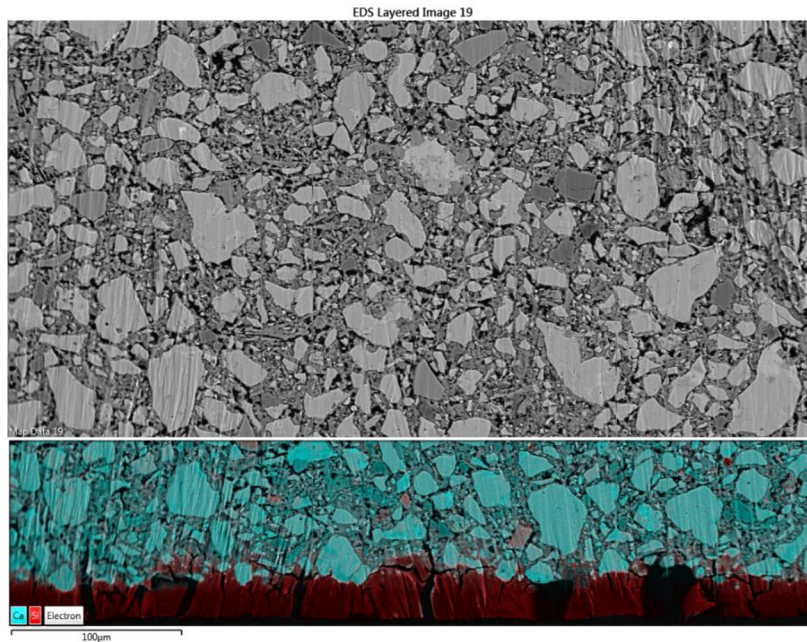


Figure 37 Overall element map of the specimen cured by potassium silicate

The onset of the interaction of lithium water glass with the cementitious substrate was recorded by imaging in the backscattered electron mode, where the occurrence of a double gel was observed, fig. 38. At the interface of the cement substrate and the residual water glass, a phase of a different colour from WG and cement can be observed. That means, that the interaction between water glass and cement surface starts on the top of the surface and then gradually penetrates to the depth of the sample.

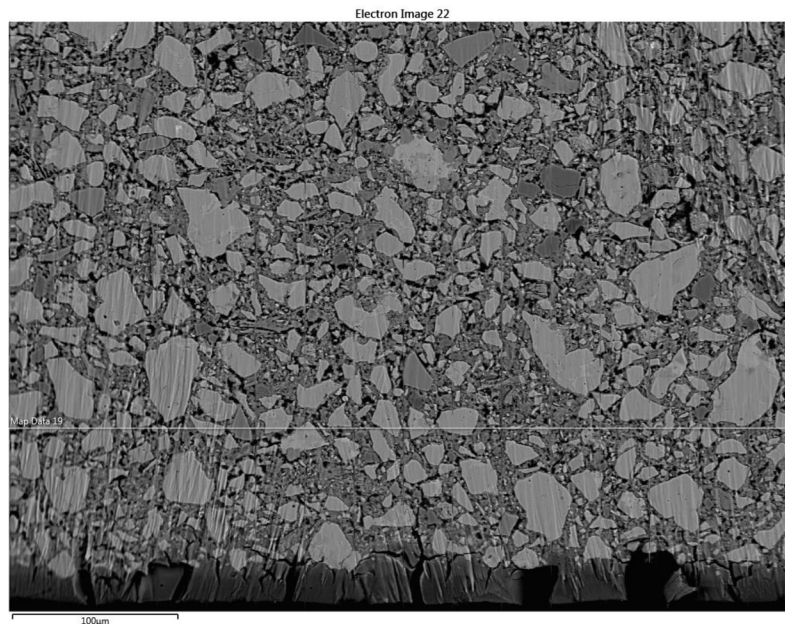


Figure 38 SEM image of the sample, cured by lithium silicate

Generally alkali silicates are likely contribute to the consumption of $\text{Ca}(\text{OH})_2$, increase the content of gel products, in addition they could reduce the Ca/Si ratio [87] also as Pan et al. report in their work [88]. So, alkali silicate could react with $\text{Ca}(\text{OH})_2$ and form more C-S-H phase, that had lower Ca/Si ratio.

Colloidal silica

The next examined sample was the sample, which was treated by the colloidal silica (with particle size about 10 nm). The biggest problem that stood in the way to the quality results was the behaviour of colloidal silica to the cement surface, where after drying on the cementitious substrate, the whole layer of colloidal silica cracked, and it is likely that there was no deeper interaction and penetration fig. 39.

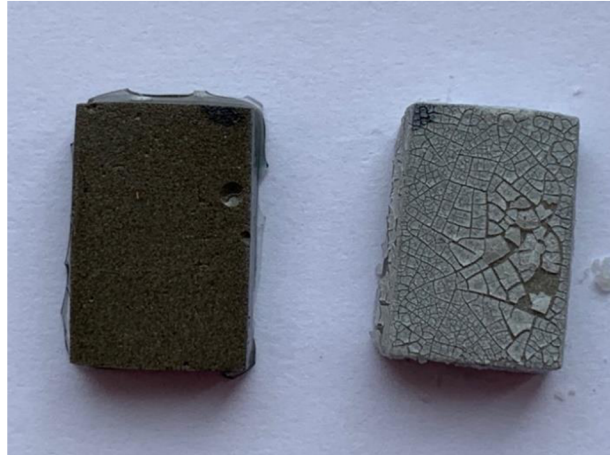


Figure 39 Appearance of samples treated with sodium water glass (left) and colloidal silica (right)

The proof of the low influence of colloidal silica on the cement surface is the distribution of Si which is shown in fig. 40.

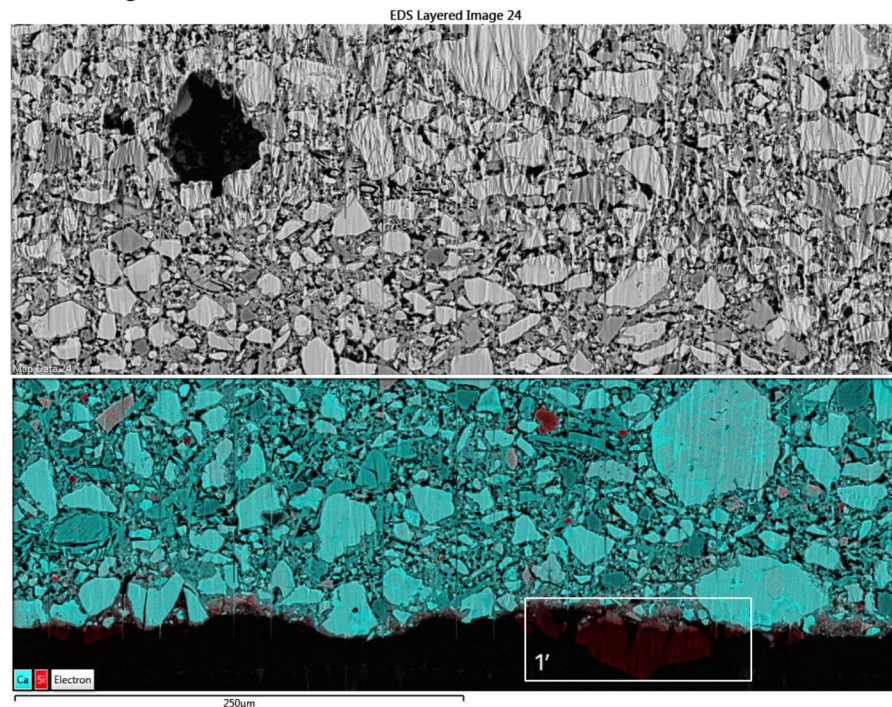


Figure 40 Overall element map of the specimen by colloidal silica treatment

The depth of penetration of Si ions is minimal, in addition it can be seen in marked detail 1' peeling off a piece of treatment agent. So, it is likely that SiO_2 from colloidal silica cannot influence deeper layers of cementitious substrate. If we refer to the chapter where the gelation time was determined, then the measurement showed that the colloidal silica immediately gels upon contact with a saturated solution of $\text{Ca}(\text{OH})_2$. It could also take place

here, when in contact with the cement surface, the colloidal silica, due to high reactivity, gels without being able to penetrate inside and affect the deeper layers in this short time.

Nevertheless, due to the SEM-EDS analysis the amount of K in colloidal silica was observed, probably potassium silicate was added as a stabilizer. As you can see in fig. 41 and fig. 42 places where K ions are observed coincides with the parts where Ca and Si ions. The penetrated layer is thin, which would correspond to the ability of potassium silicate to penetrate, that due to its large ionic radius, it is probably not able to affect the deeper layer of the cement substrate.

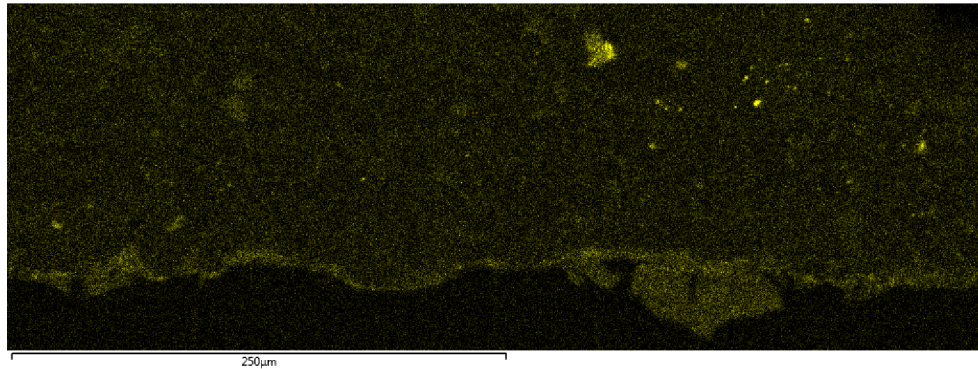


Figure 41 Distribution of K in the sample, with colloidal silica on the cement surface

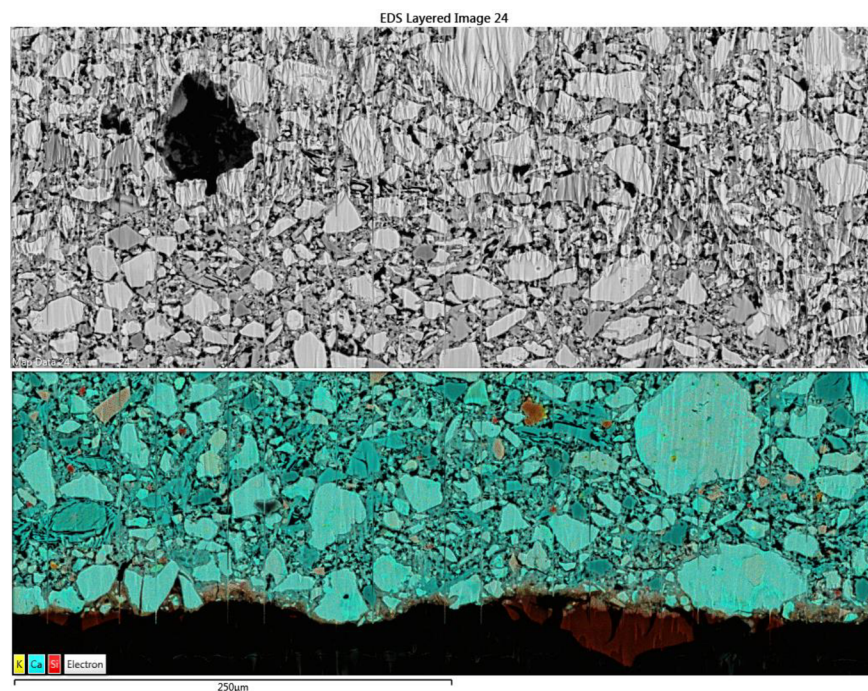


Figure 42 Overall element map of the specimen by colloidal silica treatment, together with potassium distribution

Reference with water

In the case of the reference sample treated only with pure water, neither new phases nor any drastic morphological change was expected to be observed, which was confirmed in the fig. 43. In case of this sample the water served as a reagent that should promote hydration and the formation of more C-S-H phase. In contrast to the samples treated with silicates, a uniform distribution of Si, Ca, Na and K can be seen, the alkali content in this case corresponding to the alkali contained in the cement itself. HeidelbergCement Group, with plant in Mokra in their technical sheet indicates the quantity of Na₂O and K₂O, which is shown in tab. 2 in theoretical part of the thesis. Obviously, the aim of this measurement is not to determine a quantity of

alkalis in cement, but technical sheet for the SEM-EDS image serves as a proof that present alkalis are contained in cement itself. The marked parts (1', 2', 3') in fig. 43 should correspond to the binder part, the C-S-H-gel.

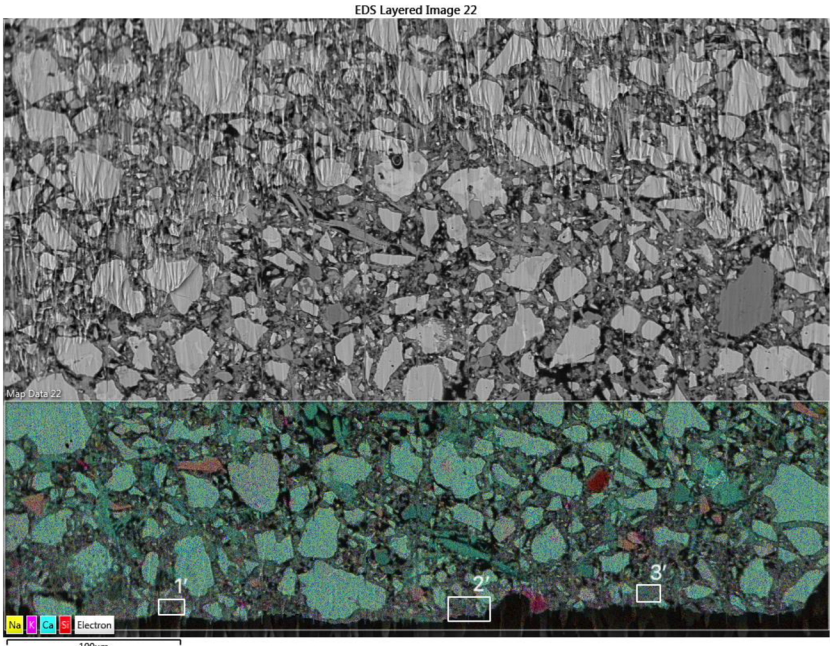


Figure 43 Overall element map of the specimen which was wetted by water

Reference

The reference sample fig. 44 which was not treated with anything, has a certain resemblance to the previous sample, which was treated with water. The same parameters already described in the previous paragraph correspond to this sample: the even distribution of alkalis, pure C-S-H phase, continuous top layer of sample (without cracks). Unfortunately, the two marked areas in fig. 44 (1' and 2') correspond to an error, that probably occurred during ion polishing, but even this problem did not stand in the way of evaluating the results.

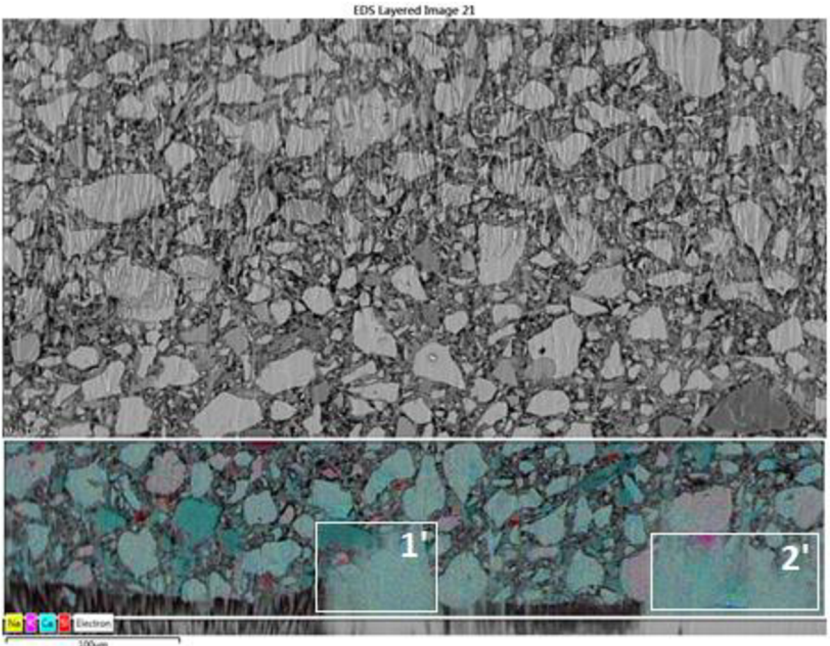


Figure 44 The overall element map of the referent sample

The above-mentioned results in this chapter can be partly summarized by the following criteria: depth of penetration, distribution of alkalis, adhesion to the cement substrate. Lithium silicate turned out to be the most capable solution which penetrated deeper and preferentially incorporated into the cement hydrated than others, because its the smallest cation. Among the alkali silicate, the potassium silicate, conversely, passed through the smallest depth of the sample. Sodium silicate took an intermediate position among alkali silicates. None of the above silicates had problems adhering to the sample.

Equally important to sum up results of influence colloidal silica on cement surface, regardless the results obtained were not satisfactory. Colloidal silica due to its high pozzolanic reaction causes immediate consumption of CH to modified form of C-S-H [89]. New formed C-S-H phase is highly polymerized and has a lower C/S ratio (1.0) [90]. For the reason of high reactivity colloidal silica reacts with CH faster, than it could penetrate deeper into the structure of the cement substrate. Nevertheless, CS appears to be a potential agent that would be able to affect the microstructure of the cement surface if high reactivity could be suppressed, for example by using surfactant agents.

The results obtained with the sample which was soaked in water and the reference sample met the expectations and did not differ significantly between each other.

6 CONCLUSION

This paper deals with the influence of selected types of silicates, specifically, potassium, sodium and lithium silicates, which are considered as a film-forming agents and colloidal silica on the cement surface. Understanding the mechanism of action of silicate on the cement surface would allow its unconditional use in various industries.

First of all, it would be appropriate to say that according to the results of all measurements, no clear, because some of them are better in some properties than others. Unfortunately, none of the tested samples stood out positively in all measurements, each had its pros and cons of interaction with the cement substrate. The samples were always divided into two groups: treated 1 (*set A*) and 24 (*set B*) hours after mixing. In general, samples from *set A* usually gave kind of non-persuasive results, and those results could not always be unambiguously evaluated. It should be also mentioned, that the effect of the care agents was assessed by measuring gelation time, water absorption, isothermal calorimetry, porosimeter and influence on the microstructure.

Based on the determination of the gelation time, it is not possible to determine which silicate was the most suitable for application as film-forming agent, because this measurement was made for the general understanding of whether the compound is able to form a gel with the presumed product of cement hydration (portlandite). In terms of gelation, all types of treatments gelled for a reasonable period of time, which could be considered a meaningful start.

The next part of the thesis was devoted to the study of the resistance of the treated concrete surface to water penetration. Firstly, the Karsten tube test (widely used in the industry) was performed. The ambiguous result *set A* could be affected by the insufficient formation of hydration products required for the reaction with silicates, with the fact that some film-forming solutions (lithium silicate and colloidal silica) were not able to form a continuous protective layer. On the contrary, *set B* provided us more lucrative results, where sodium and potassium silicates were among the best, in terms of the lowest water adsorption, followed by lithium silicate, colloidal silica and the worst obviously was the reference sample. It followed by water absorbability test, where obtained results were the similar to the trend of *set B* from the Karsten tube test. Absorbability test according to the EN 1062-3 standard was beneficial, and based on the results of this test, it was verified that alkali silicates contribute the most to the reduction of water penetration, while colloidal silica at least and reference samples absorbed the most water. Moreover, pore healing was then proven by the porosimeter test, where alkali silicate turned out to be effective pore blockers.

Furthermore, the samples were evaluated in terms of the effect of alkali on the mechanical properties (flexural and compressive strength) of concrete specimens. In terms of mechanical properties, the samples were not significantly affected. The differences between the values of samples with the film-forming treatment and reference specimen differed within the standard deviation, so it can be concluded that the treatment 24 hours after mixing did not bring dramatically positive effect on the samples strengths in the following 1, 2, 7 and 28 days.

Monitoring the hydration process of the sample was very helpful, where it was found that essentially the more alkali additions accelerated the hydration process in early age, the less hydration heat it would release over time. In both *sets A* and *B* the trends of silicates behaviour were similar; sodium silicate the most accelerated the hydration progress, conversely colloidal silicate the less, potassium and lithium silicate took the middle position.

Further, measurement of the porosity was performed, where it was shown that the treatment after 1 hour was not beneficial for filling the pores, due to the system being too fresh to form pores, so in such short time period, the treatment agents contribute to the hydration process rather than healing the pores. In contrast with fresh samples, *set B* seemed to be profitable for our study, because the difference in the porosity of the treated samples from the reference one was noticeable. The activity of alkaline silicates was apparently connected with the ionic radius

of individual elements, which accounted for the majority of these silicates, more precisely the highest efficiency was shown by potassium water glass, slightly lower sodium WG and the weakest result belonged to lithium silicate. Due to the nature of the above-mentioned water glasses, it has been assumed that lithium water glass affects a rather deeper layer, due to the small ion radius, but the larger the ion radius, the lower the water glass with such ion radius is able to penetrate into the sample. Potassium silicate had the greatest effect due to the fact that it probably closed the upper pores by reacting with hydration products on the surface without getting into a deeper layer.

The last using method which was used to monitor the microstructure influence by treatment agents was SEM-EDS analysis. This method was important in understanding of the behaviour of pore blockers solutions in terms of the degree of penetration of the monitored element, its distribution and influence on the C-S-H phase. Through this method, it has been revealed that lithium glass is most capable of affecting the deeper layer of the cement substrate (50 μm), to a lesser extent sodium (30 μm) and at least penetrating into the sample potassium water glass (10 μm). Penetration into deeper layers means a greater possibility to incorporate into the structure of the C-S-H gel and to modify it. Unfortunately, even due to its small particle size (10 nm), colloidal silica encountered the problem of precipitation on the surface of the sample because of its high puzzolanic reactivity with $\text{Ca}(\text{OH})_2$, which led to cracking of the film-forming layer and prevented its further penetration to cement substrate.

The influence and interaction between pore blockers solutions and cement surface have been discussing for many years and scientists have not yet come to a clear conclusion about the mechanism, the most appropriate time of treatment and the most effective blocker of resistance, it makes sense to continue this research.

Based on the results which was obtained in this work, it was difficult to determine the most suitable silicate for the application as the film-forming agent, each of them has their strong and weak sides. Given that the properties of the individual silicates would be mutually reinforcing, it makes sense to continue and test various mixed combinations of water glasses and colloidal silica in this work.

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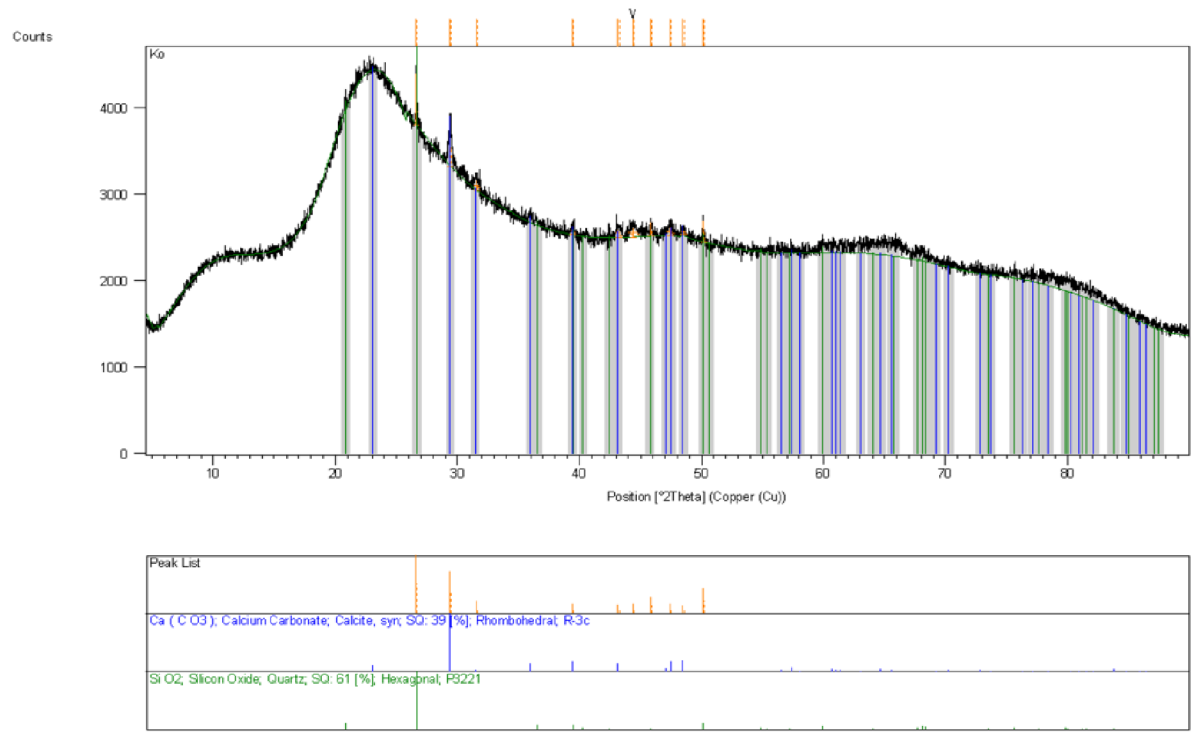
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8 LIST OF ABBREVIATION

OPC – Ordinary Portland Cement
C-S-H – Calcium Silicate Hydrate
WG – Water Glass
UV – Ultraviolet
 M_s – Silicate Modulus
AAR – Alkali-Aggregate Reaction
ASR – Alkali-Silicate Reaction
ACR – Alkali-Carbonate Reaction
C/S – CaO/SiO₂ molar ratio
Ip – Inner Product
Op – Outer Product
NMR – Nuclear Magnetic Resonance
SANS – Small-Angle Neutron Scattering
TEM – Transmission Electron Microscope
C₃S – Tricalcium Silicate
C₂S – Dicalcium Silicate
C₃A – Tricalcium Aluminate
AFt – Ettringite
CS – Colloidal Silica
CH – Portlandite
w/c – water to cement ratio
w/s – water to solid ratio
XRD – X-Ray Diffraction
SEM – Scanning Electron Microscope
SE – Secondary Electrons
BSE – Back Scattered Electrons
AE – Augers Electrons
EDS – Energy-Dispersive Spectroscopy

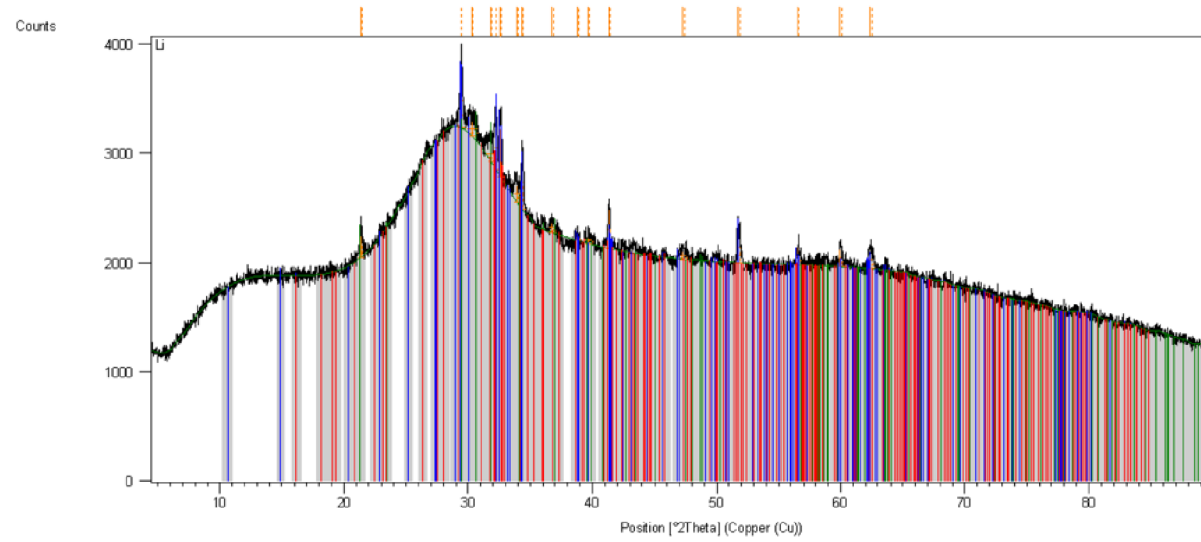
9 ATTACHMENTS

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Attachment 1 Diffractogram of colloidal silica



Phase
Ca3 Si O5; Calcium Silicon Oxide, Hstrurite, syn; SQ: 52 [%]; Monoclinic; Cm
Li2 (C O3); Lithium Carbonate, Zabuyelite, SQ: 32 [%]; Monoclinic; C2/c
Ca2 (Si O4); Calcium Silicate, Larnite, SQ: 16 [%]; Monoclinic; P21/n

Attachment 2 Diffractogram of lithium silicate