

Properties of ASTOR self-healing concrete (SHC) using PENETRON inorganic additive

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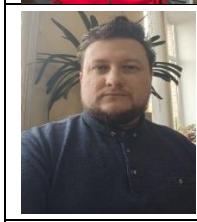
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Annotation. In modern construction, the problem of increasing the durability and reliability of concrete structures is becoming increasingly relevant. One of the promising areas is the creation of self-healing concretes with the properties of repairing microcracks during operation, which significantly extends the service life and reduces repair costs. An important aspect is the correct selection of components and technologies for their application, since the effectiveness of such materials depends not only on the introduction of special additives, but also on the consistency of the entire composition of the concrete mixture. As part of the development of an innovative product, self-healing concretes (SHC), in cooperation with LLC "ASTOR INVEST" and LLC "PENETRON UKRAINE" designed concrete with the additive "PENETRON ADMIX" was developed. The object of the study is the self-healing ability of the SHC type design concrete mixture. The following methods were used to evaluate the processes: determination of water permeability, phenolphthalein indication and structural analysis using an electron microscope. The beginning of recovery for the design composition occurs already on the 5th day, with

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a decrease in water permeability, and reaches zero after 17–22 days under pressure and without pressure. The control samples continued to pass water, despite the fact that the water permeability also decreased for them. Accordingly, the design composition with the additive has a higher degree of recovery. This crystal hydrates, which restore the

microstructure of concrete. Structural analysis confirmed that the interaction of the components contributes to the restoration of the strength and tightness of concrete. The results obtained indicate that the creation of effective self-healing concretes requires a targeted approach to the selection of the composition and technology, which takes into account the interaction of all components of the system to achieve optimal characteristics and durability.

Key words: concrete, penetron, self-healing, cracks, ettringite, waterproofing, carbonization.

INTRODUCTION

Concrete remains a key material in modern construction, serving as the basis for the construction of buildings, bridges, roads, and many other civil engineering structures worldwide [1–3]. Its widespread use is primarily due to its structural strength, durability, and relatively low cost. However, despite these advantages, concrete is inherently prone to the development of microcracks and larger cracks caused by mechanical stresses, environmental factors such as freeze-thaw cycles, chemical attacks, and constant loading on structures [1, 4]. These cracks not only compromise the integrity of the structure but also facilitate the penetration of harmful substances, accelerating deterioration processes such as reinforcement corrosion, leaching, and carbonation of cement minerals [5].

Traditional methods for maintaining and repairing cracks in concrete structures involve manual intervention, including sealing, patching, or reinforcing the structure. These processes are often labor-intensive due to the need to prepare the damaged area for restoration [6]. This, in turn, adds additional costs and typically provides only temporary solutions [7]. Furthermore, such repairs may not address the root causes of cracking, leading to repeated failures and reduced service life of infrastructure and civil structures [8–9]. Consequently, the development of innovative, autonomous repair mechanisms within concrete itself has attracted significant research interest, driven by the need for more sustainable, cost-effective, and long-lasting solutions.

Self-healing concrete (SHC) is an advanced material capable of autonomously repairing cracks and restoring its properties without external intervention [8, 10–11]. This concept draws inspiration from biological systems, where healing processes occur naturally to close open wounds or injuries. In materials science, this mechanism involves the introduction of specific agents or self-activation processes that, when cracks form, stimulate self-healing responses [12–15]. The integration of self-healing functionality aims to extend the service life of concrete structures, reduce maintenance costs, and improve overall durability by decreasing the need for resource-intensive repairs.

Research on self-healing processes in concrete has increased over the last decade, focusing on various strategies to facilitate autonomous crack repair. These include the incorporation of microcapsules containing healing agents, bacterial-based systems, mineral deposition methods, and chemical additives designed to react with ambient moisture [16]. Often, these approaches are combined to optimize recovery efficiency, durability, and ease of implementation. The underlying mechanisms of self-healing are multifaceted and largely depend on the type of additive or system used. Broadly, the mechanisms can be divided into physical and chemical processes. Physical mechanisms involve filling cracks with mineral deposits or polymer gels that physically block crack propagation pathways [17]. Chemical mechanisms involve ongoing reactions that form insoluble compounds, such as calcium carbonate, to fill and seal cracks [18].

Microcapsule-based systems are among the most widely studied approaches. They involve embedding microcapsules containing healing agents—such as epoxy resins, polymer gels, or other reactive compounds—into the concrete matrix [13–15]. When a crack propagates through the matrix and ruptures the capsules, the healing agent is released, filling the crack and initiating polymerization or other reactions to harden and restore the material's integrity.

Bacterial self-healing: Biological systems utilize bacteria that precipitate calcium

carbonate, effectively sealing cracks through mineralization processes [4, 13, 19]. These bacteria are encapsulated within the concrete or embedded in the matrix and are activated when cracks form, reacting with moisture and nutrients to produce mineral deposits that fill the cracks.

Mineral deposits: The recovery of the structure through mineral deposits depends on the internal environment of the concrete, which contains residual calcium hydroxide and other reactive compounds. When cracks allow water to penetrate, these compounds react with CO_2 or other ions from the environment to form calcium carbonate, naturally sealing the cracks over time [19].

Use of chemical additives: Some chemical additives are designed to react with moisture or other environmental stimuli, causing the formation of in situ recovery products. For example, the addition of sodium silicate can react with calcium hydroxide to form calcium silicate hydrate (C-S-H), which can fill cracks and potentially improve mechanical properties [18].

The effectiveness of self-healing mechanisms depends on numerous factors, including the type and amount of healing activator agents, their distribution within the matrix, environmental conditions, and the properties of the concrete itself. For instance, the size and distribution of micropores influence the extent and rate of healing, with uniform dispersion being critical for optimal performance [5, 16]. Additionally, activation conditions such as moisture content, elasticity, and crack width significantly affect healing efficiency.

Recent studies have highlighted that the stability and compatibility of healing agents within the cement matrix are crucial for long-term performance [20]. Furthermore, the mechanical properties of the healed zones—such as bond strength and load-carrying capacity—are important considerations when assessing the practical viability of self-healing properties [20–21].

Despite promising developments, several challenges hinder the widespread adoption of self-healing concretes. Cost remains a significant barrier, especially for biological

systems that require nutrients and bacterial cultures. Scalability and the long-term stability of regenerative agents under different environmental conditions are also critical issues [21–22]. Moreover, understanding the microstructural mechanisms and developing standardized test protocols are necessary to effectively evaluate and compare different systems. Overall, self-healing admixtures offer a transformative approach to improving the durability and resilience of concrete structures. By providing autonomous crack repair through various mechanisms, these systems have the potential to reduce maintenance costs, extend service life, and contribute to sustainable infrastructure development. Continued research to understand the underlying mechanisms, optimize material formulations, and overcome practical challenges is vital to translating laboratory successes into real-world applications.

PURPOSE AND METHODS

LLC "ASTOR INVEST" has developed the SHC design composition in cooperation with LLC "PENTRON UKRAINE". This concrete composition was designed taking into account the use of an inorganic additive with penetrating action.

The purpose of the study is to verify the effectiveness of the self-healing processes of the SHC design composition on the raw material base of Ukrainian production.

The object of the study is to study the self-healing process of the developed design composition of concrete of class C25/30 (B30) SHC with the additive "PENETRON ADMIX". The effectiveness of the composition was checked using water permeability indicators, when cracking concrete samples of various shapes, with crack sizes from 0.45 to 0.50 mm.

To achieve the goal, the following tasks were set:

- prepare a set of samples with and without additives in accordance with current norms and standards (DSTU B V.2.6-156);

- prepare hardened samples (28 days) for research by artificially creating cracks in accordance with the parameters and norms of the waterproofing and self-healing method;

- record the moment of self-healing by daily monitoring of the intensity of liquid penetration.

- study the structural properties of control and design samples using electron microscopy methods.

For the accuracy of the results, the control and design concrete samples had the same strength class C25/30 (B30). Portland cement CEM II/A-M (S-W)-500 R manufactured by Cemark was used as a binder. To obtain the appropriate strength class, the following were regulated: the content of binder, sand, crushed stone, additives, as well as the water-cement ratio. The results of water permeability indicators were taken with a frequency of 4 times a day at regular intervals. Filling the cup with a volume of 1 dm³ of water. At the same time, the time of flow of 1 dm³ of water through the crack was recorded with an accuracy of 1 second. This operation was repeated until the complete cessation of water flow through the crack.

RESULTS AND EXPLANATIONS

To ensure proper assessment and a variety of results, 8 cube samples measuring 150x150x150 mm and 12 cylindrical samples measuring 200x250 mm were prepared. The samples were divided into two groups: control—mixtures without additives—and experimental—mixture C25/30 (B30) SHC. Each group was prepared following the developed recipes for concretes of strength class C25/30 (B30), taking into account the introduction of additives and modifications to the composition and water-cement ratio.

To study the water permeability of the cube samples, an additional pressure of 0.04 atm was applied. As shown in Fig. 1, the difference between the two sets of samples is significant. The self-healing processes of the concrete mixture with additives began to manifest on the fifth day of the experiment. After that, a sharp decrease in water permeability was observed. The water permeability of the control samples remained at an average of 8 L/h for 29 days,

which represents about 15% of the volume of water used. Such stability and constancy of water flow through the cement matrix can lead to further deterioration of both the monolithic structure and the penetration of aggressive agents into the material, resulting in leaching of cement components and corrosion of the reinforcement in the structures.

For the test samples, water permeability decreased by nearly 93% by the 10th day of the experiment. By the 20th day, water flow had stopped altogether.

Thus, it can be noted that under conditions of low applied pressure, for samples with crack widths up to 0.5 mm, the self-healing processes in the SHC composition began on the fifth day of the experiment and completely restored the structure of the material by the 20th day with constant water exposure. In contrast, the control samples continued to allow water seepage, with a stable difference of 1 L/h between daily values, even after 20 days.

Unlike the cubic specimens, no additional pressure was applied to the cylindrical specimens. As with the previous cubic specimens, the concrete compositions for the cylindrical specimens had the same formulations.

When studying the cylindrical concrete specimens, water infiltration was performed using the gravity method, which resulted in significantly different experimental outcomes in terms of the water penetration rate through the thickness of the specimens. The use of this method lasted for 35 days, during which a more detailed characterization of the self-healing processes was observed.

Two groups of samples, labeled 1 to 12, were prepared according to the developed compositions. The first group consisted of SHC samples, while the second group served as the control. For both groups, the experiments continued until several consistent results were obtained. In the case of samples with the additive, no water penetration was observed.

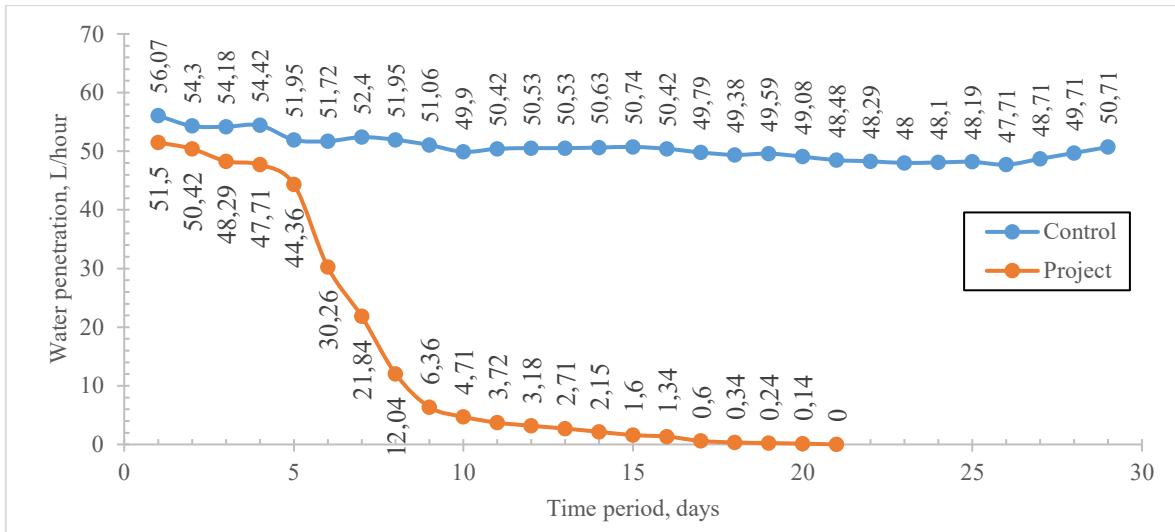


Fig. 1. Water permeability indicators of samples with (project) and without (control) additives

Analyzing the design composition in conjunction with the results obtained (Fig. 2), differences can be observed in the indicators of the rate of full restoration of structural integrity during the self-healing process. For five out of six samples, complete restoration occurred within a period of 18 to 22 days. This is reflected in the lower water penetration values (Fig. 2) of samples marked 1–6. However, it

should be noted that samples 1–3 exhibited higher average water penetration values, which can be attributed to the formation of wider cracks during sample preparation. Despite this, full restoration for these samples still occurred within the same timeframe as samples 4–6, namely 18–22 days.

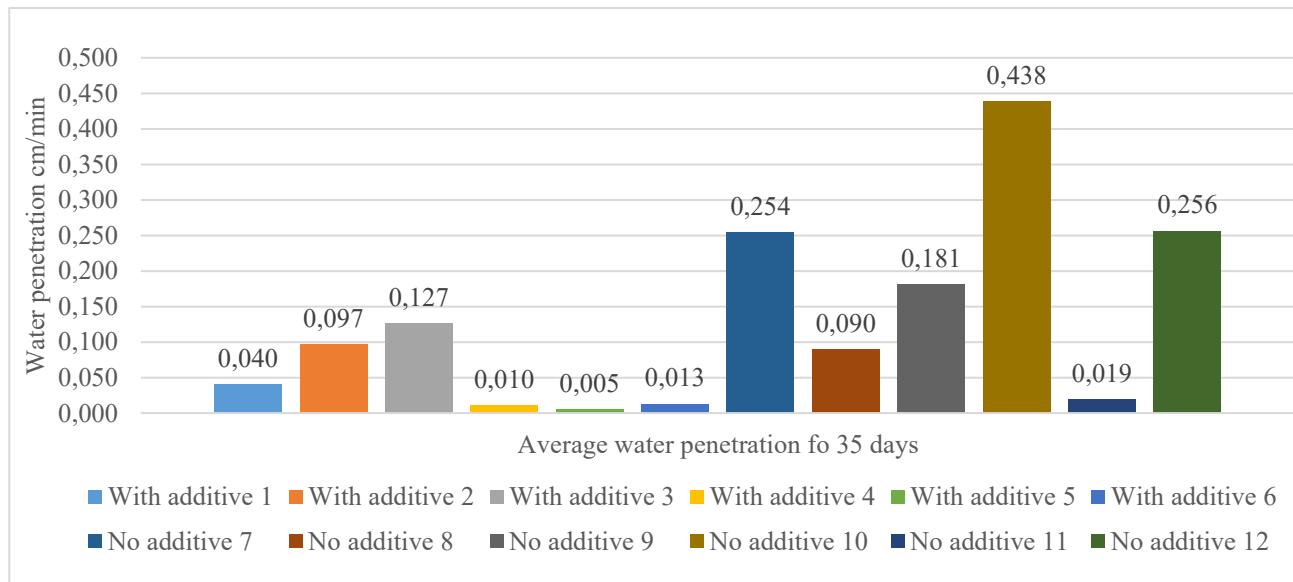


Fig. 2. Water penetration indicators for cylindrical concrete samples

For the samples without the "PENETRON ADMIX" additive (samples 6–12), the average water penetration values were significantly higher compared to the samples of the designed composition. Additionally, after a 35-day period, although the total volume of liquid

gradually decreased, the samples continued to allow water passage at a relatively constant rate. This phenomenon can be attributed to the inherent self-healing properties of cement, which are due to free calcium oxides (CaO) or other clinker components that did not undergo

complete hydration during concrete preparation. During water saturation, these minerals began to hydrate again, exhibiting a self-healing effect.

However, as the results indicate, this mechanism is not as pronounced as in the SHC samples. Furthermore, the observed decrease in water penetration in the samples without the additive may also be associated with carbonation—a form of chemical corrosion of cement in concrete. To verify this hypothesis, both SHC and control samples were examined using phenolphthalein indicator (Fig. 3).



Fig. 3. Phenolphthalein indication of cement carbonation.

The indication of samples using this method revealed a visible change in the structural pH of the concrete samples. As is well known, the hydration of cement minerals in concrete creates an alkaline environment that promotes

the growth of crystal hydrates. Therefore, using phenolphthalein indicator allows for the detection of carbonation processes within the concrete structure through a color change.

As shown in Figure 3, part of the sample after testing exhibits an intense purple color in one area, while another part displays a weak or no color change. This variation indicates that carbonation has occurred in the concrete, specifically within the cement matrix. This process is accompanied by the formation of insoluble calcium carbonate (CaCO_3) compounds, which fill microcracks and pores within the monolithic structure. While these compounds are insoluble, their presence can negatively impact the strength and integrity of the concrete. Accumulating in cracks and pores, excess CaCO_3 causes internal stresses and promotes the formation of new cracks, thereby increasing the destructive effects of water ingress. Due to its chemical inertness, as water penetration continues, CaCO_3 is gradually washed out of the structure, creating space for the formation of new compounds and leading to a gradual reduction in the material's strength.

This phenomenon is further confirmed by structural images of the samples obtained through electron microscopy (Fig. 4).

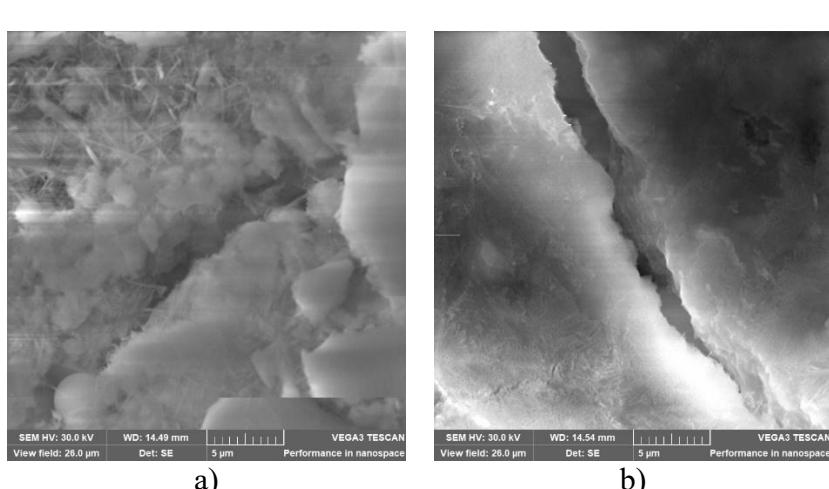


Fig. 4. Structural difference of concrete samples with additive (a) and without additive(b).

It can be seen that in the SHC design samples in the crack zone, the formation of needle-shaped crystal hydrate compounds is observed (Fig. 4, a), which are responsible for binding cement minerals and ensuring early strength,

while for samples without the additive (Fig. 4, b) they are absent.

CONCLUSIONS

During the study of the developed SHC composition in collaboration between LLC "ASTOR INVEST" and LLC "PENTRON UKRAINE," indicative characteristics of the self-healing structure of the concrete were identified. Through the application of three different methods for analyzing the physical and chemical properties of the concretes, the following indicators of the effectiveness of the compositions were revealed:

- for the first group of samples of the designed composition, which were subjected to a pressure of 0.04 atm, water permeability of the cement stone began to decrease as early as the 5th day of the experiment and was completely eliminated within the period of 17–21 days;

- control samples, under the influence of pressure, had constant indicators of water permeability and had a low difference in indicators between the beginning and the end of the experiment;

- the results of water permeability for concrete samples of the control composition, which were tested without pressure, decreased for 5-6 days, but the complete restoration of the structure did not occur. The control composition of concrete continued to pass water, but its volume and intensity decreased over a longer period than the design.

Summarizing these results, it can be concluded that in both the designed and control compositions, the reduction in water permeability is primarily due to the rehydration of cement components. However, the underlying mechanisms differ: in the control concrete, this process is associated with the presence of CaO and other unhydrated clinker components, as well as carbonation processes. In contrast, for the designed composition, the reduction is attributed to the formation of crystal hydrates. Both mechanisms are confirmed by phenolphthalein indicator tests and electron microscopy structural analysis.

Additionally, the use of the SHC additive in the designed composition appears to enhance the activation of existing cement recovery processes. It should be noted that this effect is specific to the use of CEM II/A-M (S-W)-500 R cement produced by Cemark. Therefore, it is

advisable to study systems utilizing other types of cement as binders, since the interaction between concrete components – binder, fillers, additives, and the water-to-cement ratio – determines the activation, efficiency, and progression of self-healing processes.

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бетонів вимагає цілеспрямованого підходу до підбору складу і технологій, що враховує взаємодію всіх компонентів системи для досягнення оптимальних характеристик і довговічності.

Ключові слова: бетон, пенетрон, самовідновлення, тріщини, еттрінгіт, гідроізоляція, карбонізація.

Властивості самовідновлювального бетону (SHC) компанії ASTOR з використанням неорганічної добавки PENETRON

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Аннотація. У сучасному будівництві дедалі більш актуальною стає проблема підвищення довговічності та надійності бетонних конструкцій. Одним із перспективних напрямків є створення самовідновлювальних бетонів із властивостями до відновлення мікротріщини під час експлуатації, що значно подовжує термін служби та зменшує витрати на ремонт. Важливим аспектом є правильний підбір компонентів та технологій їх застосування, оскільки ефективність таких матеріалів залежить не лише від введення спеціальних добавок, а й від узгодженості всього складу бетонної суміші. У рамках розробки інноваційного продукту, самовідновлювальних бетонів (SHC), при співпраці ТОВ «АСТОР ІНВЕСТ» і ТОВ «ПЕНЕТРОН УКРАЇНА» розроблено проектний бетон із добавкою «PENETRON ADMIX». Об'єктом дослідження є самовідновлювальна здатність проектної бетонної суміші типу SHC. Для оцінки процесів застосовували методи: визначення водопроникності, фенолфталеїнову індикацію та структурний аналіз за допомогою електронного мікроскопа. Початок відновлення для проектного складу відбувається вже на 5-й день, зі зниженням водопроникності, і досягає нуля через 17–22 день під тиском та без тиску. Контрольні зразки продовжували пропускати воду, не дивлячись на те що водопроникність і для них теж зменшувалася. Відповідно, проектний склад з добавкою володіє більшою ступінню відновлення. Цей механізм пов'язаний з утворенням кристалогідратів, які відновлюють мікроструктуру бетону. Структурний аналіз підтверджив, що взаємодія компонентів сприяє відновленню міцності та герметичності бетону. Отримані результати, вказують на те, що створення ефективних самовідновлюючих