

The object of this study was the concrete structures of a chemical enterprise for the production of titanium dioxide. In this case, the ore is decomposed with sulfate acid according to the sulfate production technology. In an aggressive environment, chemical corrosion of concrete occurs, prolonged over time.

Using X-ray diffraction and X-ray fluorescence analysis methods, the mineral composition of two prototypes of concrete was determined. It was found that the sample obtained from the workshop for processing ore with sulfate acid showed an increased content of sulfur oxide (SO₂) on the surface, by 33 %, with a reduced content of carbonates (CaCO₃) on the surface, by 52.9 %, at a depth of 2 cm – by 53.65, compared to another (control) sample. At the same time, iron oxide (Fe₂O₃) was found on the surface in a sample of concrete from the ore storage room (control), the content of which decreased by 10.4 % at a depth of 2 cm, and by 12.4 % at a depth of 4 cm.

The results of electron microscopy show sulfur crystals on the surface of a concrete sample. It was also found that the microstructure of concrete was changed under the influence of sulfate corrosion, depending on the intensity of the exposure to a depth of 2 to 4 cm. By the method of thermoprogammed mass spectrometry, it was established that when a sample of concrete exposed to sulfate acid is heated to a temperature of 400 °C, sulfur dioxide SO₂ is released mainly from the surface. From the surface of the control sample, which contains a significant amount of CaCO₃, which is easily destroyed by sulfate acid, there is probably a smaller amount of the product of thermal destruction of calcium carbonate carbon dioxide (CO₂).

The results of the experiment can be used to study the mechanism of development of sulfate corrosion of concrete prolonged over time

Keywords: sulfate technology, X-ray diffraction, thermoprogammed mass spectrometry, X-ray fluorescence analysis, electron microscopy

UDC 614.48:631.223

DOI: 10.15587/1729-4061.2022.268627

DETERMINING CHANGES IN THE MINERAL COMPOSITION OF CONCRETE DUE TO CHEMICAL CORROSION IN A SULFATE ENVIRONMENT

Oksana Shkromada

Corresponding author

Doctor of Veterinary Sciences, Professor
Department of Obstetrics and Surgery **

E-mail: oshkromada@gmail.com

Viktoriia Ivchenko

PhD, Associate Professor*

Vadym Chivanov

Doctor of Agrarian Sciences, Associate Professor

Department of Radiation Biophysics
Institute of Applied Physics, National Academy
of Sciences of Ukraine

Petropavlivska str., 58, Sumy, Ukraine, 40000

Oiha Shvets

PhD, Associate Professor*

Department of Therapy, Pharmacology,
Clinical Diagnostics and Chemistry**

Volodymir Moskalenko

Chief Engineer of Complex Installation
Department of Nuclear-Physical Research***

Alexander Kochenko

Junior Researcher

Department of Radiation Biophysics***

Olena Babenko

PhD, Associate Professor

Department of Human Biology, Chemistry and Methodology of Teaching Chemistry
Sumy State Pedagogical University named after A. S. Makarenko

Romenska str., 87, Sumy, Ukraine, 40002

Yuliya Kharchenko

PhD, Associate Professor

Department of Human Biology, Chemistry and Methodology of Teaching Chemistry
Sumy State Pedagogical University named after A. S. Makarenko

Romenska str., 87, Sumy, Ukraine, 40002

Alina Pikhtirova

PhD, Associate Professor

Department of Public Health
Sumy State University

Rymskoho Korsakova str., 2, Sumy, Ukraine, 40007

Oksana Yurchenko

PhD, Associate Professor

Department of Construction and Operation of Buildings, Roads and Road Constructions**

*Department of Therapy, Pharmacology, Clinical Diagnostics and Chemistry**

**Sumy National Agrarian University

Herasyma Kondratieva str., 160, Sumy, Ukraine, 40021

***Institute of Applied Physics, National Academy of Sciences of Ukraine

Petropavlivska str., 58, Sumy, Ukraine, 40000

Received date 18.09.2022

How to Cite: Shkromada, O., Ivchenko, V., Chivanov, V., Shvets, O., Moskalenko, V., Kochenko, A., Babenko, O., Kharchenko, Y., Pikhtirova, A.,

Accepted date 01.12.2022

Yurchenko, O. (2022). Determining changes in the mineral composition of concrete due to chemical corrosion in a sulfate environment. East-

Published date 30.12.2022

ern-European Journal of Enterprise Technologies, 6 (6 (120)), 42–50. doi: <https://doi.org/10.15587/1729-4061.2022.268627>

1. Introduction

Studies that address the problem of long-term chemical corrosion of concrete (35 years) are very important in terms of the operational capacity of building structures, as well as

understanding the processes occurring during the destruction of cement stone.

For the production of titanium dioxide by the sulfate method at chemical plants, titanium-containing slags, as well as ilmenite concentrates, are used as raw materials.

Titanium dioxide (TiO_2) pigment is different, depending on the technique of its production, it may differ in crystal structure and pigment properties. Basically, TiO_2 is used for the paper, paint and varnish, plastic and rubber industries as a pigment. It is known that the production of titanium dioxide occurs according to sulfate and chloride technology. With chloride technology, the amount of waste is much less. Most enterprises that produce TiO_2 using sulfate technology face an issue related to a large amount of waste. At the experimental enterprise, ilmenites are used as raw materials – FeTiO_3 , titanomagnetite – $[\text{TiFe}_2\text{O}_3 + \text{Fe}_3\text{O}_4]$, with a ratio of $\text{FeO}/\text{Fe}_2\text{O}_3$ less than 2, hematitioilmenite – $\text{FeTiO}_3 \cdot \text{Fe}_2\text{O}_3$, with a ratio of $\text{FeO}/\text{Fe}_2\text{O}_3$ less than 2. Such ilmenite concentrates are used from the Irshinsky, Norwegian, Bukin, and Fedorivske deposits of the Zhytomyr oblast. These concentrates, using sulfate technology for the production of titanium dioxide, are decomposed by sulfate acid. Most of the waste is salts of iron and sulfate acid. Therefore, the conditions of production where these compounds form in large quantities and enter the air of the workshop are quite toxic and destructive relative to concrete structures.

In the study, the results of the destructive activity of chemical corrosion in a sulfate environment. Structural changes in concrete were studied using electron microscopy at different depths from the sample surface. The mineral composition of various concrete samples was also determined by X-ray fluorescence analysis, which gives an idea of the chemical processes that occurred over time during the direct interaction of the components of concrete with H_2SO_4 . As a confirmation of the change in the qualitative composition of concrete and its heat resistance, the method of thermoprogrammable mass spectrometry (TPD MS) was used. During the destruction of concrete, changes occur at the molecular level, which can be assessed during the X-ray structural studies. The method shows the intact crystalline phases of concrete samples.

An integrated approach to the study of the effects of chemical corrosion makes it possible to determine the depth of concrete damage, the results of structural micro- and macroscopic changes, and the mineral composition. This is necessary to predict the period of safe and environmentally sound operation of industrial premises of chemical enterprises.

The relevance of appropriate research relates to the need to determine the depth and mechanism of chemical corrosion of concrete under the conditions of the sulfate environment of a chemical enterprise.

2. Literature review and problem statement

Titanium dioxide is the basis for the formation of other compounds, including metallic titanium. Titanium dioxide is used more often as a mineral paint, filler in the production of metal and rubber.

The production of titanium dioxide can occur by sulfate and chlorine techniques. Chlorine extraction method is safer from an environmental point of view, owing to the use of improved technology, which is carried out under a continuous mode using full automation of production [1]. However, the disadvantage of this method is the greater requirements for the purity of raw materials, the use of corrosion-resistant equipment.

They apply the sulfate method for the production of titanium dioxide, which involves the use of a large amount of H_2SO_4 . Also, the process cannot be fully automated, so people are involved in the process. Since the process is not carried out in a completely closed system, a significant amount of sulfate acid enters the outside and reacts with the concrete structures of the enterprise. Paper [2] investigated the mechanism of destruction of concrete under the action of SO_2 . However, the studies were conducted under artificial laboratory conditions, so it is difficult to predict sulfate carbonization in real conditions prolonged over time.

In most tests [3, 4], researchers try to protect the concrete surface from chemical corrosion but for each object it is necessary to create specific protection for concrete structures, depending on the environment.

The study of changes in the properties of concrete under the influence of sulfate corrosion is an important problem for predicting the characteristics and durability of concrete. Studies [5, 6] show that sulfate ions from the environment enter into a chemical reaction with concrete components. Penetration into concrete occurs due to the flow of diffusion, adsorption, and convection processes. The paper carried out modeling of accelerated sulfate corrosion in the «dry-wet» cycle. It was found that there is a relationship between reducing the strength of concrete and the depth of its damage. The experiment did not take into account the temperature and time of exposure to sulfate corrosion.

In [7], it was found that corrosion of concrete in the sewage system is caused by a high concentration of H_2S in wastewater. The researchers proved that cement directly reacts with sulfate acid, which was formed as a result of the oxidation of H_2S without the participation of microorganisms that oxidize sulfide. The limitation of the study is that the experiment was carried out in the field, which was created in a specific environment of the sewer system, which cannot guarantee the presence of similar conditions in other hydrotreatment systems.

Researchers [8] found that bacteria of the genus *Thiobacillus* in the process of metabolism are able to convert hydrogen sulfide into sulfuric acid, which reacts with concrete and forms gypsum. As a result of this process, there is a decrease in the strength of concrete and its destruction. The results of the work prove the relationship between the amount of sulfur and exposure, with compressive strength, weight loss, porosity, and corrosion. The disadvantage of the study is that the experiment did not consider the effect of the corrosion process on the mineral composition of concrete.

A test study was carried out to measure the strength of concrete in close cross sections parallel to the corrosive surface by ultrasonic using exponential heads [9]. The samples were obtained from an object that was subjected to sulfate corrosion for five years, which is too short a period to predict prolonged chemical corrosion.

In livestock facilities, the main building material is concrete, which is constantly exposed to biochemical corrosion. The aggressive environment of livestock facilities, as shown by studies [10], is associated with microorganisms, the use of high concentrations of disinfectants and natural animal feces. The researchers determined the effect of interrelated biochemical corrosion on concrete structures but did not study the detailed mechanisms of physicochemical changes and the depth of corrosion processes.

Paper [11] proposed a method for assessing corrosion damage to sulfate concrete using computed tomography, ultrasonic measurement, and an analytical hierarchical process. The proposed methods give fairly accurate results and analytics methods, compared to traditional ones. However, the equipment used is very specific, expensive, and the process is time consuming.

Over time, the characteristics of concrete can change under the influence of the external environment. Diffusion and reaction of H_2SO_4 with concrete components is a complex physicochemical process. Products that occur when interacting with sulfate acid transform concrete [12].

There are no data on the changes in mineral composition and depth of damage prolonged over time sulfate corrosion of concrete. Researchers [13] are concerned with this issue and have created a mathematical model (stochastic kinetic equation) to establish the likely development of a sulfate corrosion reaction leading to the formation of corrosion products. The model can be used to predict corrosion trends and the effect of sulfate corrosion products on the durability of concrete. However, the method provides only probabilistic information.

Based on the analysis of previous experiments, it became necessary to study in more detail the sulfate corrosion of concrete in a chemical enterprise, prolonged in time. At the same time, experiments should include studies of the trace element composition, microstructure, and heat resistance of concrete subjected to destructive changes. The results will make it possible to prove the relationship between the change in the microelement composition and the violation of the structure of concrete. In addition, the study of the mechanism of sulfate corrosion of concrete is the basis for predicting the depth of corrosion in the environment of H_2SO_4 .

3. The aim and objectives of the study

The aim of our study is to determine the relationship of the degree of intensity of chemical corrosion with the depth and changes in the mineral composition of concrete in the sulfate environment of a chemical enterprise. This will determine the intensity of the development of chemical corrosion over time in a sulfate environment. Based on the results of analyzes of concrete samples by modern physicochemical methods, the prospect of conducting a reasonable prediction of the stability of production facilities over a given period of time arises.

To accomplish the aim, the following tasks have been set:

- to determine the mineral and phase composition of concrete under sulfate conditions by X-ray diffraction and X-ray fluorescence analysis;
- to investigate the presence of microstructural and chemical components of changes in concrete under the influence of a sulfate medium using electron microscopy and to conduct a comprehensive thermal analysis of concrete samples by the method of thermoprogrammed mass spectrometry.

4. Materials and research methods

4. 1. Object and conditions of research

The idea of the experiment was that under the conditions of a sulfate-aggressive environment of a chemical enterprise

for the production of titanium dioxide, structures are exposed to prolonged corrosion, which leads to a change in the microstructure, elemental composition, and heat resistance of concrete. Therefore, for a comprehensive study of concrete samples, the method of X-ray fluorescence analysis, thermoprogrammable mass spectrometry, scanning electron microscopy, and X-ray diffraction were involved. Subsequently, patterns and justifications for the data obtained were established.

The object of our study is concrete in the titanium dioxide production workshop.

The subject of the study is the regularities of physicochemical changes in concrete under the influence of sulfate chemical corrosion prolonged over time.

The main hypothesis of the study was that based on the determination of structural changes and mineral composition, it is possible to predict the depth of destruction, structural and chemical changes in concrete.

The research was carried out at a chemical enterprise for the production of titanium dioxide by the sulfate method. Concrete samples were obtained in a workshop for the production of titanium dioxide from different depths: surface; 2.0 cm; 4.0 cm. A depth of 4 cm is actually the bottom of a concrete sample.

Laboratory tests were carried out in the laboratory of architecture and engineering surveys at Sumy National Agrarian University, and the laboratory of the Department of Radiation Biophysics of the Institute of Applied Physics of the NAS of Ukraine during 2021–2022 (Sumy, Ukraine).

4. 2. Procedure of research using an X-ray fluorescent analyzer

Concrete samples were examined using the X-ray fluorescent analyzer (XFA) ProSpector 3 (Elvateh, Kyiv, Ukraine). The XFA method is based on the registration of the characteristic X-ray radiation of the atoms of the experimental substance, which occurs as a result of irradiation of the sample with X-ray tube radiation. The analytical unit of the device was fixed at a distance of 1.5 mm from the surface of the concrete sample for 30–60 s. Measurement of the intensity of the characteristic radiation of atoms allows one to calculate the concentration of the corresponding element.

4. 3. Procedure for determining the heat resistance of concrete using thermoprogrammable mass spectrometry

To determine the heat resistance of concrete samples, the method of thermoprogrammable mass spectrometry (TPD MS) was used; the installation includes a high-temperature furnace and the gas mass spectrometer MX-7304 (VAT SELMI, Sumy, Ukraine). Concrete samples weighing 5–10 mg were heated in vacuum from 40 to 900 °C at a rate of 15 °C/min. At the same time, gases formed during heating were registered. Gases were identified by molecular weights (m/z): H_2O – 18 a.o.m., CO_2 – 44 a.o.m. 64 – SO_2 a.o.m. [14].

4. 4. Procedure of scanning electron microscopy

The study of the microstructure of concrete samples was carried out by scanning electron microscopy on the raster electron microscope (REM) 106 (VAT SELMI, Sumy, Ukraine). To establish corrosive changes in the microstructure of concrete, the samples were fixed on metal

bedding using double-sided carbon tape. To give samples electrical conductivity, silver was sprayed. For the study of biofilms of microorganisms, concrete samples were fixed with 2.5 % glutaraldehyde at 0.2 M phosphate buffer solution, dehydrated in a series of ethyl alcohols of increasing concentration and sprayed with silver [15]. It was investigated in a raster electron microscope under the mode of secondary electrons in the range of electron-optical magnifications from 200 to 5,000 times.

4. 5. Procedure of X-ray diffractometry research DRON 4-07 in Nifiltered $K\alpha$

Structural studies of the samples were performed on the DRON 4-07 X-ray diffractometer in Nifiltered $K\alpha$ copper anode radiation. The shooting was carried out in the range of angles of 2θ from 200 to 800, where 2θ is the Bragg angle. Before the study, concrete samples were crushed and ground in a mortar to a size of 15–20 microns, and then pressed into a retainer. The studies used X-ray focusing according to Bragg-Brentano [16].

5. Results of the study of chemical corrosion of concrete

5. 1. Results of determining the mineral composition of concrete by X-ray diffraction and X-ray fluorescence analysis

Two samples of concrete obtained at a chemical plant for the production of titanium dioxide by the sulfate method were investigated. Concrete sample No. 1 (control) was obtained in the ore storage room – ilmenite concentrates. A study was conducted to determine the mineral composition of concrete using an X-ray fluorescent analyzer (Tables 1, 2).

Table 1

Results of studying the mineral composition of concrete sample No. 1 using an X-ray fluorescent analyzer

Indicator	Surface	Depth 2 cm	Depth 4 cm
	Value, %		
CaO	71.40±1.70	79.10±1.30	79.60±0.60
Fe ₂ O ₃	22.20±1.60	11.80±1.00	9.80±0.50
SiO ₂	4.60±0.40	6.50±0.40	8.80±0.30
Al ₂ O ₃	0.60±0.30	0.40±0.30	0.34±0.15
Sb ₂ O ₃	0	1.50±1.4	0.60±0.60
SO ₂	0.54±0.04	0	0.25±0.01
MnO	0	0	0.40±0.17
CrO	0.35±0.08	0	0
PbO	0.12±0.24	0.40±0.30	0
ZrO ₂	0.11±0.09	0.17±0.10	0
SrO	0	0.16±0.07	0.17±0.03

As a result of the study, it was found that a significant amount of calcium oxide (CaO) was found on the surface of concrete sample No. 1 (control), while on the surface the content of calcium oxide was 7.7 % less compared to a depth of 2 and 4 cm. The usual component of the con-

crete mix, silicon dioxide (SiO₂) was found in a sufficient amount in the concrete sample, but less on the surface compared to the deep layers, by 1.9 %. Iron oxide (Fe₂O₃) was found in large quantities on the surface, then, deep into the concrete sample, the content of the element progressively decreased by 10.4 % and by 12.4 %. Sulfur oxide (SO₂) was found on the surface of concrete in small quantities.

Concrete sample No. 2 was obtained in the workshop for the production of titanium dioxide by the sulfate method, namely in the room where ilmenite concentrates are treated with sulfate acid. The results of determining the trace element composition of concrete sample No. 2 are given in Table 2.

Table 2

Results of studying the mineral composition of concrete sample No. 2 using an X-ray fluorescent analyzer

Indicator	Surface	Depth 2 cm	Depth 4 cm
	Value, %		
CaO	18.50±0.90	25.50±1.20	79.40±0.80
Fe ₂ O ₃	16.00±0.40	15.40±0.40	8.50±0.40
SiO ₂	20.70±0.90	21.90±1.00	7.11±0.23
Al ₂ O ₃	4.30±1.40	5.90±1.50	0.51±0.12
Sb ₂ O ₃	0.10±0.15	0	0
SO ₂	33.40±0.70	27.10±0.70	0
K ₂ O	2.80±0.80	1.5±1.10	2.00±0.90
MgO	2.00±4.00	0	0
MnO	0.16±0.006	0.14±0.08	0.35±0.14
P ₂ O ₅	0.90±0.50	1.60±0.60	0
TiO ₂	0.50±0.30	0.40±0.30	1.40±0.70
Cr ₂ O ₃	0.09±0.07	0.13±0.09	0
SrO	0.09±0.01	0.12±0.01	0.31±0.03
PbO	0	0.04±0.05	0.04±0.03

Based on the results obtained, calcium oxide on the sample surface is smaller, leveled with deeper layers by 7 % and 60.9 %. This result indicates the corrosion processes that occurred on the surface of the concrete, as a result of which a significant part of the calcium present in concrete in the form of calcium carbonate was lost. The level of iron oxide (Fe₂O₃) on the sample surface was twice as high compared to 4 cm deep, indicating the penetration of the element from the environment. Also characteristic of this sample was a high content of sulfur oxide (SO₂), 33 % more compared to sample No. 1 (control). Penetration of sulfur oxide was observed from the surface up to 2 cm, with a decrease of 6.3 %. Silicon dioxide (SiO₂) in this sample was in a large amount on the sample surface, which decreased at a depth of 4 cm by 13.59 %.

Also, to clarify the results, an X-ray diffractogram of powdered sample No. 1 (control) and No. 2 (experimental) concrete was acquired (Fig. 1, 2).

The sample is dominated by calcium carbonate CaCO₃, which indicates the preservation of the basic composition of concrete and its non-significant chemical corrosion, as shown by subsequent studies by REM and TPD MS.

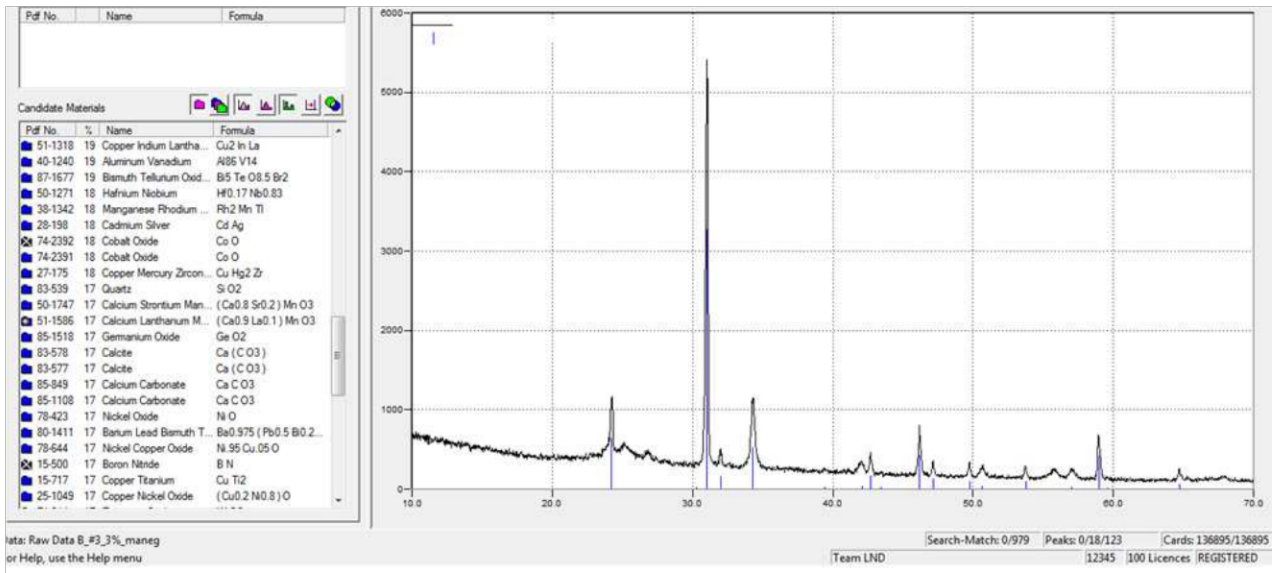


Fig. 1. The results of the study of concrete sample No. 1 (control) using an X-ray diffractometer

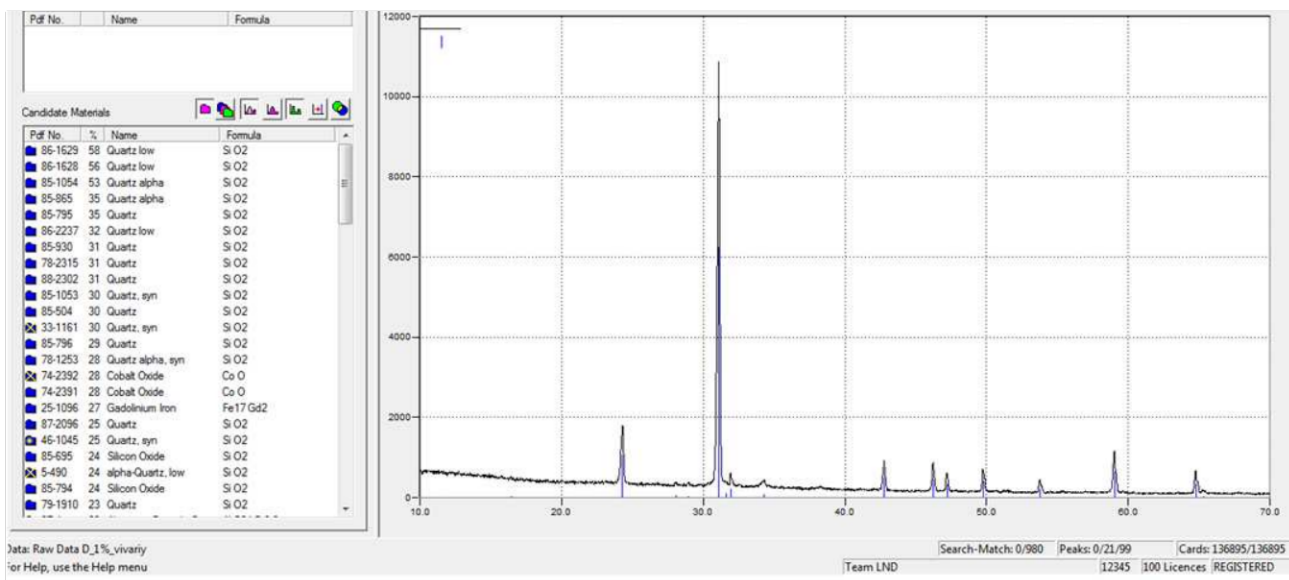


Fig. 2. The results of the study of concrete sample No. 2 (experimental) using an X-ray diffractometer

In the results obtained from X-ray structural studies, silicon oxide (SiO_2) prevails in sample No. 2. Peaks in Fig. 2 characterize the crystalline phases of parts of non-destroyed concrete samples. In sample No. 2, calcium carbonate is destroyed, as a result of which it does not have a normal crystalline structure, so it is absent on the X-ray diffractogram.

5. 2. The results of the study of microstructural changes using mass spectrometry and electron microscopy

To determine structural changes in concrete samples under the influence of chemical corrosion, concrete samples were subjected to heating to 1000 °C (Fig. 3, a, b).

As a result of the study of concrete samples using the TPD MS method, it was found that at a temperature of 100 °C with an intensity of 1.0–1.2, water evaporated from the surface and a depth of 2 cm. From this, we can conclude that the water content is probably higher in concrete sample No. 2 (experimental) destroyed by the action of sulfate acid.

At a temperature of 600 °C, a significant amount of CO_2 was released from the surface of concrete sample No. 2 (Fig. 4, a, b), which indicates the presence in the sample of a significant amount of calcium carbonate (CaCO_3) and which is consistent with the results of the mineral composition (Table 1).

From a depth of 2 and 4 cm, the intensity of carbon monoxide release was 0.10–0.12 a.u. When the prototype was heated, carbon monoxide was not released from the sample surface; from a depth of 2 cm, the intensity of CO_2 release was 0.10 a.u., from a depth of 4 cm – 0.18 a.u. It can be seen that the control contains a much larger amount of CaCO_3 in the surface layer of the sample than that in the prototype.

The results of the study of the control sample by the method of thermoprogrammed mass spectrometry show that from the surface, a depth of 2 and 4 cm, at a temperature of 900 °C, SO_2 released with an intensity of 0.0040 to 0.0050 a.u. (Fig. 5, a, b).

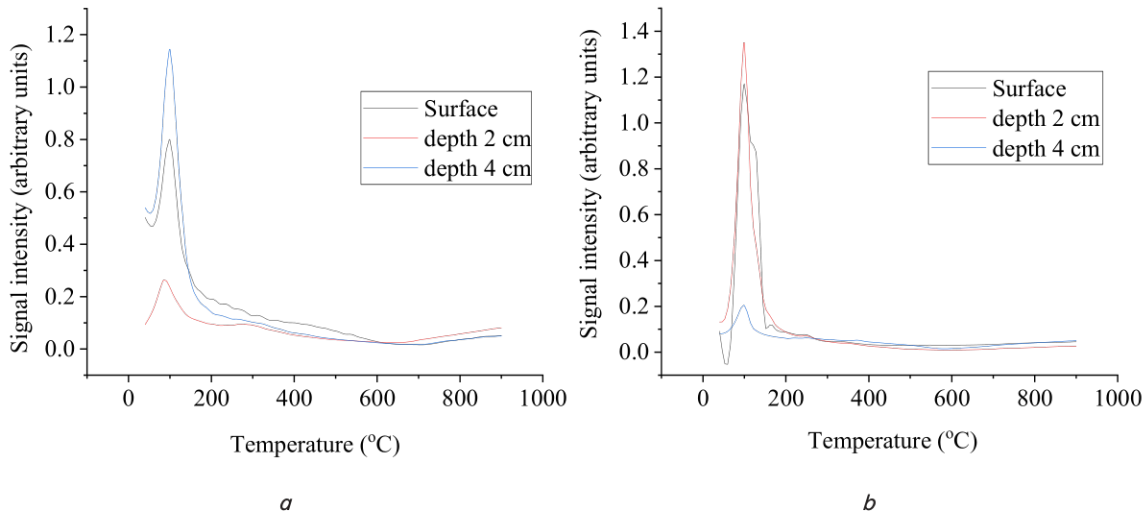


Fig. 3. Thermal graphs of H₂O release ($m/z=18$): *a* – from concrete sample No. 1 (control); *b* – from concrete sample No. 2 (experimental)

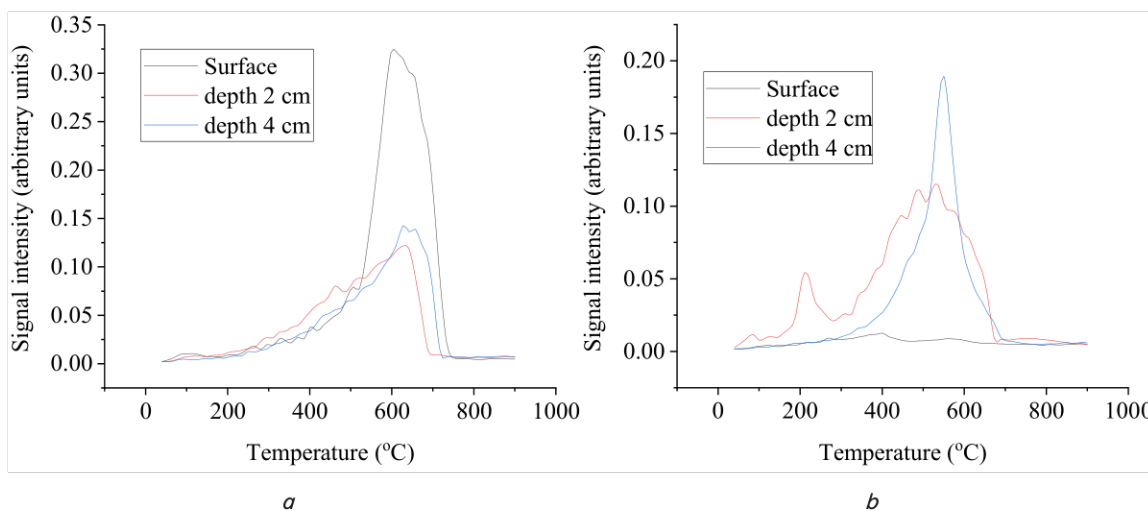


Fig. 4. Thermal graphs of CO₂ release ($m/z=44$): *a* – from concrete sample No. 1 (control); *b* – from concrete sample No. 2 (experimental)

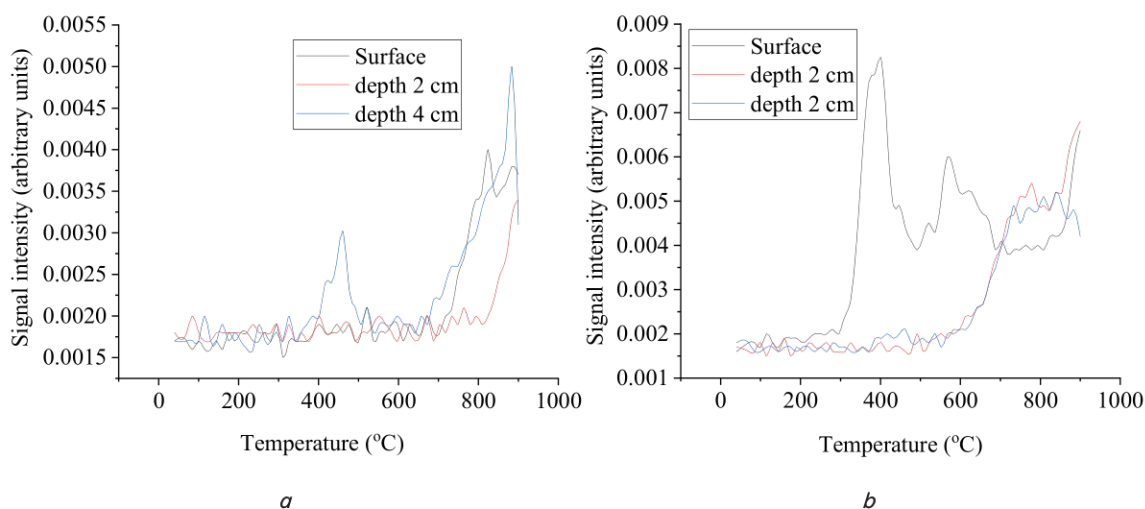


Fig. 5. SO₂ release thermograms ($m/z=64$): *a* – from concrete sample No. 1 (control); *b* – from concrete sample No. 2 (experimental)

When heating sample number 2 (experimental) Fig. 5, *b* to a temperature of 400 °C, sulfur dioxide is released from the sample surface with an intensity of 0.008. Sulfur dioxide is released from the prototype with an intensity of 0.007 from a depth of 2 cm when heated to a temperature of 800 °C. Thus, it is proved that under the action of sulfate acid, most of the sulfur is concentrated on the surface and near-surface layers of concrete.

Raster electron microscopy was used to study the micro-structure of concrete samples (Fig. 6–9).

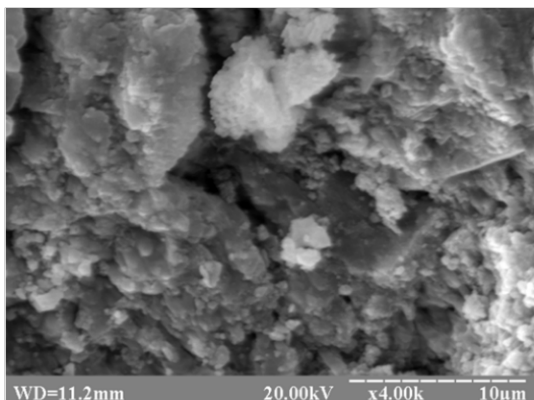


Fig. 6. Electron microscopy of the surface of sample No. 1 (control), insignificant signs of a change in the structure

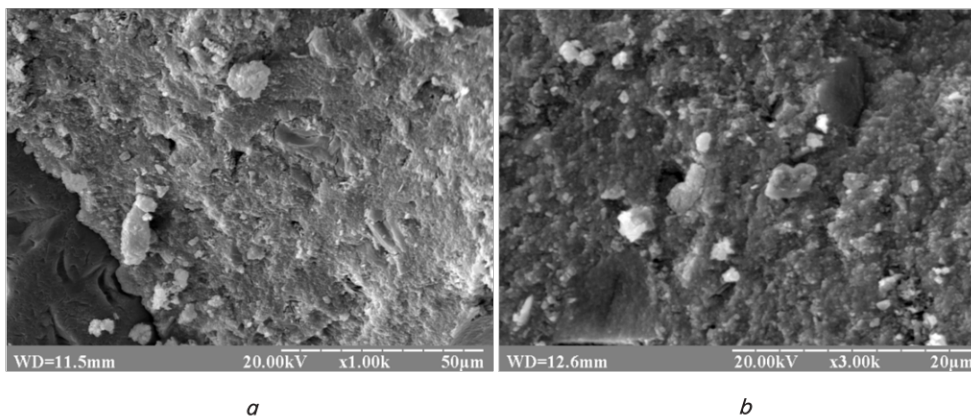


Fig. 7. Electron microscopy of sample No. 1 (control): *a* – depth, 2 cm; *b* – depth, 4 cm, no signs of corrosion

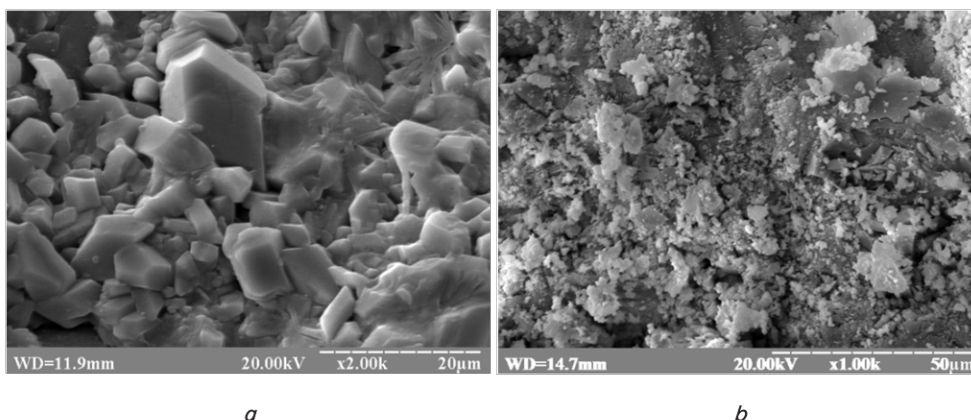


Fig. 8. Electron microscopy of the sample of the image of sample No. 2 (experimental): *a* – sulfur crystals on the surface; *b* – corrosion of the concrete surface at a depth of 2 cm

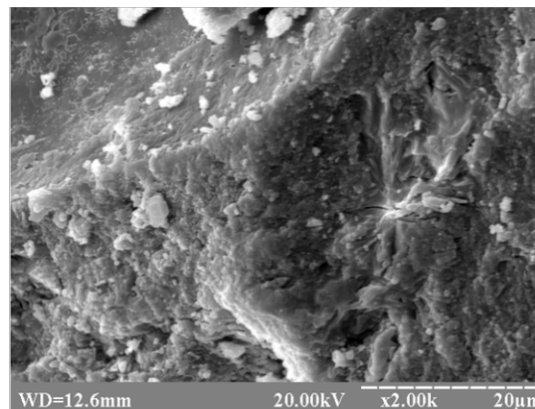


Fig. 9. Electron microscopy of the sample of the image of sample No. 2 (experimental) at a depth of 4 cm, no corrosion

Fig. 4 shows the surface of sample No. 1 (control); with violation of the integrity of the structure under the influence of chemical corrosion.

However, at a depth of 2 and 4 cm, signs of corrosion are not observed (Fig. 7, *a, b*). Thus, during long-term operation, the sample of concrete No. 1 underwent insignificant corrosion, which manifests itself only on the surface.

On the surface of concrete sample No. 2 (experimental), signs of chemical degradation of concrete with the formation of sulfur crystals were found (Fig. 8, *a*), which is confirmed by previous studies (Fig. 2, *a*).

Also, at a depth of 2 cm, there are signs of micro destruction of concrete (Fig. 8, *b*). The study of sample No. 2 at a depth of 4 cm confirms the cessation of corrosion processes in concrete (Fig. 9).

As a result of the study by REM method, it was found that concrete samples No. 1 (control) and No. 2 (experimental) had different degrees and depths of destructive processes. The prototype was negatively influenced by external environmental factors, which had their differences associated with the technological processes of titanium dioxide production in a chemical plant.

6. Discussion of results of the study of biochemical corrosion of concrete

Studies of the mineral composition have established that a large amount of carbonates (CaCO_3)

(Table 1) was found in concrete sample No. 1 (control) obtained in the premises for storing ilmenite ore, which is confirmed by TPD MS method (Fig. 2, *a*). In the sample of concrete No. 2 (experimental), obtained in the workshop for the production of titanium dioxide, on the surface of the sample, carbon monoxide was not released when heated (Table 2, Fig. 2, *b*). The study of the mineral composition of the sample indicates a decrease in the CaO content on the surface, by 52.9%, at a depth of 2 cm – by 53.65, compared to sample No. 1. At a depth of 4 cm, the level of calcium oxide content is the same in both samples, which brings chemical corrosion of the surface layer of concrete to a depth of 4 cm. Researchers [17] reported similar results as a result of corrosion of concrete in the pigsty room, when the result of destruction was the loss of calcium carbonate.

Iron oxide (Fe_2O_3) was found in larger quantities in sample No. 1 on the surface, by 6.2%, compared to sample No. 2.

In sample No. 1, traces of sulfur oxide (SO_2) were found on the concrete surface (Table 1). In the study of the mineral composition of sample No. 2, it was found, on the surface, 33.40%, and at a depth of 2 cm – 27.10%, which is confirmed by TPD MS method (Table 2, Fig. 3, *a, b*). Studies [18, 19] proved the destructive prolonged effect of sulfate acid on concrete structures in chemical plants in the production of titanium dioxide by sulfate method.

The X-ray diffractogram of powdered sample No. 1 (control) is dominated by calcium carbonate (CaCO_3), which confirms the preservation of chemical and structural integrity (Fig. 1). X-ray diffractogram of sample No. 2 (experimental) contains a large amount of silicon oxide (SiO_2), which is associated with chemical corrosion of concrete. At the same time, calcium carbonate was destroyed, which turned into gypsum [20]. As a result of sulfate corrosion, significant destruction of concrete to a depth of 4 cm occurred. In works [21, 22], laboratory studies proved that concrete samples under the influence of sulfate acid had a large number of microcracks and the destroyed corrosive layer had a tendency to fall off.

Studies of the microstructure of concrete with the help of REM revealed a violation of the integrity of the surface (Fig. 4) and the preservation of the normal structure of the cement stone at a depth of more than 2 cm (Fig. 5, *a, b*) in sample No. 1 (control). Sulfur crystals were found [23] on the surface of concrete sample No. 2 and signs of corrosion to a depth of 2 cm (Fig. 6, *a, b*), which is confirmed by other studies. At a depth of 4 cm, in sample No. 2 (experiment), the normal microstructure of concrete is preserved (Fig. 7).

There is a regularity in the reported research results associated with the intensity of penetration of chemical corrosion deep into concrete [24].

Owing to the use of a set of modern research methods, such as the X-ray diffractometric method, REM, TPD MS, and XFA, we confirm results to make it possible to predict the safe life of concrete structures. The use of modern methods and samples of concrete, which were subjected to sulfate corrosion in real conditions, is an advantage of this study over similar ones [25].

Our experiment can serve as an example of chemical corrosion of concrete, which is caused by sulfate acid at a

chemical plant for the production of titanium dioxide using sulfate technology.

The limitation of the experiment is that the samples that were investigated were obtained from a room where specific conditions for prolonged exposure to sulfate acid on concrete structures were created.

The disadvantage of the study is that it is quite difficult to obtain similar results of concrete corrosion in the laboratory, due to the creation of specific conditions for changes in temperature, humidity, and exposure to sulfate acid vapors.

The area of further research is to determine a way to reduce the effect of chemical corrosion on concrete structures in chemical plants.

7. Conclusions

1. The method of X-ray diffraction and X-ray fluorescence analyzer were used to establish the mineral composition of concrete. Our results prove that with active sulfate corrosion of the concrete sample, the content of sulfur oxide (SO_2) increases while the carbonate content (CaO) decreases. On the X-ray diffractogram of a concrete sample that is affected by sulfate corrosion in the absence of calcium carbonate (CaCO_3), there is silicon oxide (SiO_2) in large quantities, which is an integral element of ordinary sand.

2. By using electron microscopy, it was established that the microstructure of concrete is changed under the influence of sulfate corrosion and can reach a depth of 2 and 4 cm, depending on the intensity and time of destruction. On the surface of the sample, which is obtained in the workshop for the production of titanium dioxide by the sulfate method, sulfur crystals are observed, when the sample is heated to a temperature of 400 °C, sulfur dioxide is released from the surface with an intensity of 0.008. The TPD MS method confirmed the change in the ionic composition of concrete and the depth of destruction in prototypes on the surface, and the return to normal composition at a depth of 2 to 4 cm, as indicated by the content of CO_2 .

Conflicts of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

Financing

The study was conducted without financial support.

Data availability

All data are available in the main text of the manuscript.

References

1. Siryi, A. Yu. (2020). Vyrobnystvo pihmentnoho dvookysu tytanu sulfatnym sposobom. Rozrobty ta modernizuvaty vakuum-vyparnyi aparat dla kontsentruvannia rozchynu tytanilsulfatu. Sumy: SumDU, 76. Available at: <https://essuir.sumdu.edu.ua/handle/123456789/82160>

2. Niu, D., Lv, Y., Liu, X., Chen, L., Chen, G., Zhang, B. (2020). Study on the Sulfuration Mechanism of Concrete: Microstructure and Product Analysis. *Materials*, 13 (15), 3386. doi: <https://doi.org/10.3390/ma13153386>
3. Shkromada, O., Paliy, A., Yurchenko, O., Khabot, N., Pikhitirova, A., Vysochin, I. et al. (2020). Influence of fine additives and surfactants on the strength and permeability degree of concrete. *EUREKA: Physics and Engineering*, 2, 19–29. doi: <https://doi.org/10.21303/2461-4262.2020.001178>
4. Landa-Sánchez, A., Bosch, J., Baltazar-Zamora, M. A., Croche, R., Landa-Ruiz, L., Santiago-Hurtado, G. et al. (2020). Corrosion Behavior of Steel-Reinforced Green Concrete Containing Recycled Coarse Aggregate Additions in Sulfate Media. *Materials*, 13 (19), 4345. doi: <https://doi.org/10.3390/ma13194345>
5. Zhou, Y., Tian, H., Sui, L., Xing, F., Han, N. (2015). Strength Deterioration of Concrete in Sulfate Environment: An Experimental Study and Theoretical Modeling. *Advances in Materials Science and Engineering*, 2015, 1–13. doi: <https://doi.org/10.1155/2015/951209>
6. Zhao, G., Shi, M., Fan, H., Cui, J., Xie, F. (2020). The influence of multiple combined chemical attack on cast-in-situ concrete: Deformation, mechanical development and mechanisms. *Construction and Building Materials*, 251, 118988. doi: <https://doi.org/10.1016/j.conbuildmat.2020.118988>
7. Li, X., O'Moore, L., Song, Y., Bond, P. L., Yuan, Z., Wilkie, S. et al. (2019). The rapid chemically induced corrosion of concrete sewers at high H₂S concentration. *Water Research*, 162, 95–104. doi: <https://doi.org/10.1016/j.watres.2019.06.062>
8. Marquez-Peñaranda, J. F., Sanchez-Silva, M., Husserl, J., Bastidas-Arteaga, E. (2015). Effects of biodeterioration on the mechanical properties of concrete. *Materials and Structures*, 49 (10), 4085–4099. doi: <https://doi.org/10.1617/s11527-015-0774-4>
9. Stawiski, B., Kania, T. (2019). Examining the Distribution of Strength across the Thickness of Reinforced Concrete Elements Subject to Sulphate Corrosion Using the Ultrasonic Method. *Materials*, 12 (16), 2519. doi: <https://doi.org/10.3390/ma12162519>
10. Shkromada, O., Fotina, T., Petrov, R., Nagorna, L., Bordun, O., Barun, M. et al. (2021). Development of a method of protection of concrete floors of animal buildings from corrosion at the expense of using dry disinfectants. *Eastern-European Journal of Enterprise Technologies*, 4 (6 (112)), 33–40. doi: <https://doi.org/10.15587/1729-4061.2021.236977>
11. Liu, D., Gong, C., Tang, Y., Jian, Y., Cao, K., Chen, H. (2022). Evaluation of Corrosion Damage in Sulfate-Attacked Concrete by CT, Ultrasonic Pulse Velocity Testing and AHP Methods. *Sensors*, 22 (8), 3037. doi: <https://doi.org/10.3390/s22083037>
12. Ariza-Figueroa, H. A., Bosch, J., Baltazar-Zamora, M. A., Croche, R., Santiago-Hurtado, G., Landa-Ruiz, L. et al. (2020). Corrosion Behavior of AISI 304 Stainless Steel Reinforcements in SCBA-SF Ternary Ecological Concrete Exposed to MgSO₄. *Materials*, 13 (10), 2412. doi: <https://doi.org/10.3390/ma13102412>
13. Li, T., Huang, H.-H. (2021). Probabilistic quantitative analysis on the contents of sulfate corrosion products in concrete. *Construction and Building Materials*, 275, 122134. doi: <https://doi.org/10.1016/j.conbuildmat.2020.122134>
14. Murphy, C. J., Ardy Nugroho, F. A., Härelind, H., Hellberg, L., Langhammer, C. (2020). Plasmonic Temperature-Programmed Desorption. *Nano Letters*, 21 (1), 353–359. doi: <https://doi.org/10.1021/acs.nanolett.0c03733>
15. Bozhokina, M. S., Bozhokova, S. A., Rubel, A. A., Sopova, J. V., Nashchekina, Y. A., Bilyug, N. B., Khotin, M. G. (2021). Specificities of Scanning Electron Microscopy and Histological Methods in Assessing Cell-Engineered Construct Effectiveness for the Recovery of Hyaline Cartilage. *Methods and Protocols*, 4 (4), 77. doi: <https://doi.org/10.3390/mps4040077>
16. Calvin, J. J., Kaufman, T. M., Sedlak, A. B., Crook, M. F., Alivisatos, A. P. (2021). Observation of ordered organic capping ligands on semiconducting quantum dots via powder X-ray diffraction. *Nature Communications*, 12 (1). doi: <https://doi.org/10.1038/s41467-021-22947-x>
17. Shkromada, O., Fotina, T., Dudnyk, Y., Petrov, R., Levytska, V., Chivanov, V. et al. (2022). Reducing the biogenic corrosion of concrete in a pigsty by using disinfectants. *Eastern-European Journal of Enterprise Technologies*, 4 (6 (118)), 57–66. doi: <https://doi.org/10.15587/1729-4061.2022.263310>
18. Shkromada, O., Pikhitirova, A., Chivanov, V., Ivchenko, V., Sribniak, N., Shvets, O., Litsman, Y. (2022). Detection of the synergetic influence of chemical and microbiological factors on the properties of concrete constructions at chemical plants during the long-term service. *EUREKA: Physics and Engineering*, 4, 114–126. doi: <https://doi.org/10.21303/2461-4262.2022.002485>
19. Tan, Y., Yu, H., Ma, H., Zhang, Y., Wu, C. (2017). Study on the micro-crack evolution of concrete subjected to stress corrosion and magnesium sulfate. *Construction and Building Materials*, 141, 453–460. doi: <https://doi.org/10.1016/j.conbuildmat.2017.02.127>
20. Gu, Y., Martin, R.-P., Omikrine Metalssi, O., Fen-Chong, T., Dangla, P. (2019). Pore size analyses of cement paste exposed to external sulfate attack and delayed ettringite formation. *Cement and Concrete Research*, 123, 105766. doi: <https://doi.org/10.1016/j.cemconres.2019.05.011>
21. Zhao, W., Fan, Z., Li, X., Kong, L., Zhang, L. (2022). Characterization and Comparison of Corrosion Layer Microstructure between Cement Mortar and Alkali-Activated Fly Ash/Slag Mortar Exposed to Sulfuric Acid and Acetic Acid. *Materials*, 15 (4), 1527. doi: <https://doi.org/10.3390/ma15041527>
22. Zhao, G., Shi, M., Guo, M., Fan, H. (2020). Degradation Mechanism of Concrete Subjected to External Sulfate Attack: Comparison of Different Curing Conditions. *Materials*, 13 (14), 3179. doi: <https://doi.org/10.3390/ma13143179>
23. Li, J., Zhao, G., Shi, M. (2020). Degradation and life prediction model for piles due to crystallisation attack in sulfate saline area. *Advances in Cement Research*, 32 (4), 181–195. doi: <https://doi.org/10.1680/jadcr.18.00147>
24. Zhao, G., Li, J., Han, F., Shi, M., Fan, H. (2019). Sulfate-induced degradation of cast-in-situ concrete influenced by magnesium. *Construction and Building Materials*, 199, 194–206. doi: <https://doi.org/10.1016/j.conbuildmat.2018.12.022>
25. Shkromada, O., Ivchenko, V., Chivanov, V., Tsyhanenko, L., Tsyhanenko, H., Moskalenko, V. et al. (2021). Defining patterns in the influence exerted by the interrelated biochemical corrosion on concrete building structures under the conditions of a chemical enterprise. *Eastern-European Journal of Enterprise Technologies*, 2 (6 (110)), 52–60. doi: <https://doi.org/10.15587/1729-4061.2021.226587>