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SCANNING ELECTRON MICROSCOPY AND X-RAY MICROANALYSIS OF THE CONDITION OF CONCRETE STRUCTURES OF A CHEMICAL ENTERPRISE WITH LONG-TERM CORROSION IN A SULFATE ENVIRONMENT

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Abstract: Long-term operation of premises in aggressive environments of chemical enterprises affects the surfaces of concrete structures and leads to the formation of destructive processes.

The aim of the study was to determine changes in the structure and mineral composition of concrete during long-term operation in an aggressive sulfate environment at a chemical plant for the production of titanium dioxide using the sulfate method to predict the service life of concrete structures.

It has been established that during the production of TiO_2 pigment by the sulfate method, the ore is decomposed by sulfate acid at high temperature, accompanied by the release of H_2SO_4 vapor, sulfur dioxide SO_2, hydrogen sulfide H_2S and elemental sulfur. Studies have established that sulfate corrosion leads to the formation of sulfur and iron oxides on the concrete surface. Studies have revealed vast areas of the surface covered with crystals of elemental sulfur, the contents of which are confirmed by the results of X-ray microanalysis. The sizes of sulfur crystals in the image range from 12 to 180 μm, the shape corresponds to the rhombic allotropic modification S_8. The penetration depth of iron sulfates into the thickness of concrete is about 50 microns. The microstructure of the surface is loose, with signs of corrosion.

Exposure to a high concentration of sulphate acid vapors in the workshop of the enterprise led to the destruction of calcium carbonate and the formation of gypsum crystals in concrete. The formation of gypsum crystalline hydrates provokes sulfate corrosion of concrete, resulting in the formation of pores and microcracks in concrete with the formation of calcium hydrosulfoaluminate.

The studies carried out using scanning electron microscopy and X-ray microanalysis make it possible to investigate the structural changes and mineral composition of concrete under the influence of long-term sulfate corrosion.

Keywords: sulfate acid, durability of concrete, sulfur crystals, iron oxide, calcium carbonate crystals.

1. Introduction

Concrete is the material most commonly used due to its advantages in fast curing, affordable price and durability. However, in aggressive environments, the behavior of cement stone is unpredictable due to the occurrence of various chemical reactions on its surface. Temperature fluctuations, high humidity, alkaline and acidic environments can lead to destructive changes in concrete.

Studies [1, 2] show that sulfate corrosion is one of the factors affecting the service life of concrete. Experimental studies have shown that with an increase in the concentration of sodium sulfate solution, the strength of concrete decreases. With an increase in the erosion period, the strength grade of concrete decreases proportionally. However, studies were carried out in the laboratory using instruments to determine the compressive strength and changes in electrical resistance.

Studies of the microstructure and changes in the mineral composition of concrete samples under the influence of long-term sulfate corrosion have not been carried out. Also, in laboratory conditions it is impossible to reproduce real conditions, especially during long-term operation of concrete structures.

In [3], ICT (industrial computed tomography) and NMR (nuclear magnetic resonance) methods were used to study the porous structure of concrete in a sulfate medium. Scientists have found that the compressive strength in different concentrations of media first increases and then decreases, and the dry-wet cycle accelerates sulfate erosion. The study did not take into account temperature fluctuations and the influence of the sulfate environment, the concentration of which is not constant.

The process of corrosion of concrete, which was immersed in a concentrated sulfate medium, was studied [4, 5]. Microstructural and mineral methods were used to determine changes in concrete. The results prove that the process of degradation of monolithic concrete is much more active than prefabricated. Scientists in their studies did not take into account temperature and humidity differences in the actual operating conditions of concrete structures.

Scientists also propose to take into account the chemical and physical effects of sulfates, since chemical corrosion products and crystallization hydrates were found in degraded concrete [6]. Using the method of X-ray fluorescence analysis of the content of elements, it was found that sulfate ions penetrate deep into the concrete, which leads to its serious damage. However, studies conducted in laboratory conditions cannot take into account all the factors that can affect concrete structures in real operating conditions.

The aim of research is to determine changes in the structure and mineral composition of concrete during long-term operation in an aggressive sulfate environment at a chemical plant for the production of titanium dioxide using the sulfate method to predict the service life of concrete structures.

To achieve the aim, the following objectives were set:

– study of changes in the structure of concrete;

– determination of the mineral composition of the concrete sample.

2. Methods

The studies were carried out in the electron microscopy laboratory of the Sumy National Agrarian University (Sumy, Ukraine). A chemical enterprise located in the city of Sumy, Ukraine was chosen as the base for obtaining concrete samples. Samples of concrete were taken from the walls in the workshop for the production of titanium dioxide, which has been in operation for about 40 years. The enterprise uses the sulphate method for producing titanium dioxide, the technology of which consists in processing raw materials (ilmenite concentrate) with sulphate acid at a concentration of 91.5–95 % at high temperature. The release of vapors of sulphate acid and its derivatives create aggressive conditions that determine the course of acid and sulphate corrosion of the concrete structures of the workshop. The microstructure and mineral state of the surface of concrete walls have been studied.

To assess the corrosion changes in the structure of concrete, a scanning electron microscope REM 106 i (JSC SELMI, Sumy, Ukraine) was used [7]. Concrete samples were fixed on metal substrates with double-sided carbon tape. To impart electrical conductivity to the samples, the surface was covered with a layer of coal in a VUP-5 vacuum universal post (JSC "SELMI" , Sumy, Ukraine). Images were received in the mode of secondary electrons (SE) at a magnification from 100 to 5000 times. The linear dimensions of the image elements were determined using the microscope software and the digital image analysis program Digimizer. The mass fraction of chemical elements in local areas of the samples and averaged from the field of view was determined using a SEM 106 and X-ray microanalysis using the energies of the characteristic X-ray peaks. The contents of the elements were calculated in elemental and oxide form using the Magallanes electron microscope program.

3. Results and discussion

Long-term operation of reinforced concrete structures in aggressive environments of chemical enterprises affects the state of concrete surfaces and certainly leads to the development of corrosion processes. Signs of corrosion on the concrete walls in the titanium dioxide production shop were noticeable even with visual inspection as a change in the color of the surface of individual areas from light gray to yellow and dark red. To study the nature of this phenomenon, samples were taken (**Fig. 1**) and the state of the microstructure of the surface and side chip of concrete and the content of chemical elements were studied.

Fig. 1. Typical view of concrete samples from the walls of the shop for the production of titanium dioxide by the sulfate method

In the production of TiO_2 pigment by the sulphate method, titanium-containing raw materials are decomposed by sulphate acid at high temperature. The chemistry of the process of decomposition of titanium-containing slags includes the transformation:

$$4Ti_2O_3 + H_2SO_4 = 8TiO_2 + H_2S, \quad (1)$$

$$Ti_2O_3 + H_2SO_4 = 2TiO_2 + SO_2 + H_2O, \quad (2)$$

$$2H_2S + SO_2 = 3S + H_2O. \quad (3)$$

This process is accompanied by the release of H_2SO_4 vapor, sulfur dioxide SO_2, hydrogen sulfide H_2S, and elemental sulfur [8].

Studies have revealed vast areas of the surface covered with crystals of elemental sulfur (**Fig. 2**), the contents of which are confirmed by the results of X-ray microanalysis (**Fig. 3**). The sizes of sulfur crystals in the image range from 12–180 μm, the shape corresponds to the rhombic allotropic modification S_8.

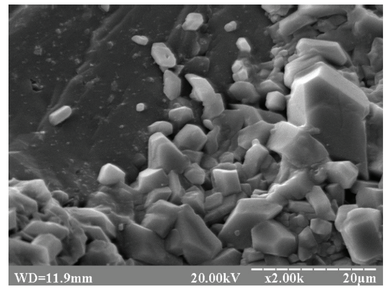


Fig. 2. Electron microscopic image of rhombic crystals of sulfur S_8. Deposition of elemental sulfur on concrete surfaces

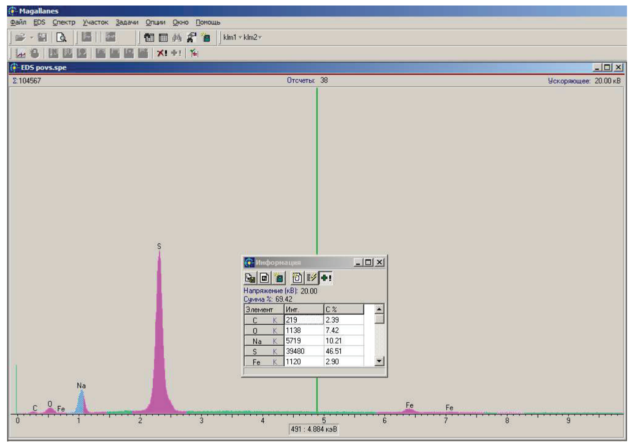


Fig. 3. The spectra of X-ray energy dispersive analysis are averaged from the microfield

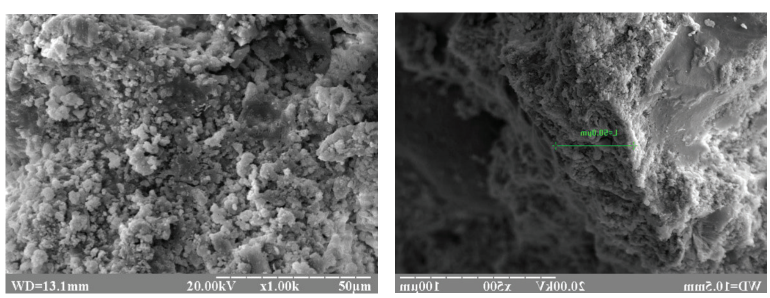
Ilmenite concentrate for the pigment industry may contain ilmenite (Fe TiO_3), titanomagnetite [$Ti{\cdot}Fe_2O_3$+Fe_3O_4] and hematoilmenite $FeTiO_3$ Fe_2O. When grinding raw materials, it is difficult to avoid air pollution with the smallest fractions of ilmenite concentrate containing iron oxides.

Sulfate acid vapors and lobules containing iron oxides condensed on the surface of the walls can cause the formation of iron sulfates:

$$FeO + H_2SO_4 = FeSO_4 + H_2O, \quad (4)$$

$$Fe_2O_3 + 3H_2SO_4 = Fe_2(SO_4)_3 + 3H_2O. \quad (5)$$

In some of the samples, the concrete surface had a reddish color, typical for iron (III) compounds. The surface microstructure is loose, with signs of corrosion (**Fig. 4, *a***). The penetration depth of iron sulfates into the concrete thickness is about 50 μm (**Fig. 4, *b***). X-ray microanalysis from the surface microfield indicates the presence of sulfur and iron oxides (**Fig. 5**).



a *b*

Fig. 4. Electron microscopic image of the surface of concrete with a high content of iron (III) salts: *a* – frontal view; *b* – side chip

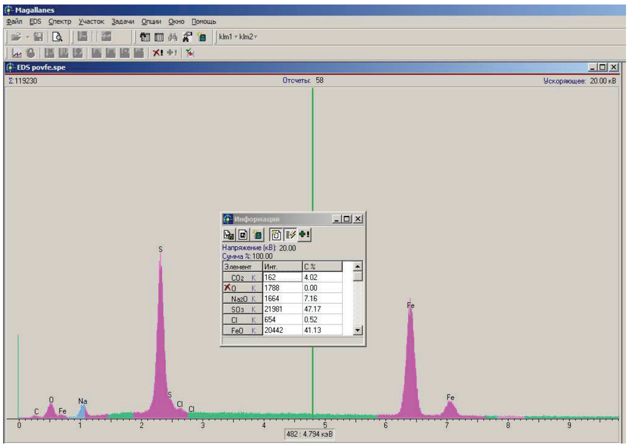


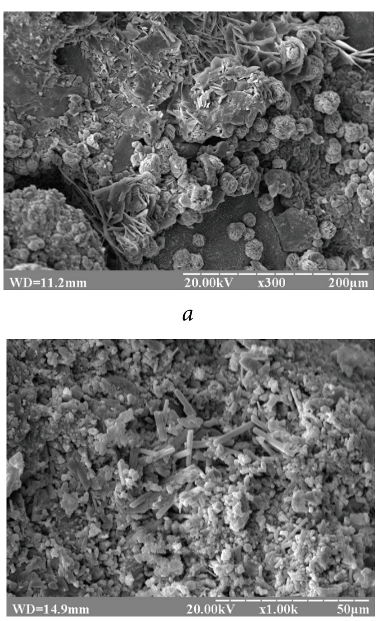
Fig. 5. The spectra of X-ray energy dispersive analysis are averaged from the microfield

The study of samples of light gray areas of the surface showed the deposition of calcium carbonate crystals (**Fig. 6, *a***), the appearance of which the researchers [9] associate with the phenomenon of concrete self-healing, as a result of lime carbonization in pores and microcracks:

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O. \quad (5)$$

Calcium carbonate can precipitate in the form of three crystalline forms (vaterite, aragonite and calcite). A number of studies simulated the conditions of $CaCO_3$ crystallization in laboratory conditions depending on the presence of foreign ions, which can contribute to the formation of metastable phases [10, 11].

The authors of [12] argue that the presence of high concentrations of sulfate ions in the crystallization medium promotes the formation of $CaCO_3$ in the form of vaterite.



a

b

Fig. 6. Electron microscopic image of the concrete surface: *a* – deposition of calcium carbonate crystals; *b* – formation of gypsum crystals in the pores of concrete

The long-term high concentration of sulphate acid vapors in the workshop of the enterprise leads to the gradual destruction of calcium carbonate as a result of acid corrosion with the formation of gypsum crystals (**Fig. 6, *b***) in the pores of concrete:

$$CaCO_3 + H_2SO_4 = CaSO_4 + CO_2 + H_2O. \quad (6)$$

The formation of gypsum crystal hydrates ($CaSO_4 \cdot H_2O$) provokes sulfate corrosion of concrete. As a result, calcium hydrosulfoaluminate ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}31H_2O$ – ettringite) is formed in the pores and microcracks of concrete. The volume of ettringite crystals increases, which causes internal stress and destruction of the cement stone [13]:

$$3CaO \times Al_2O_3 \cdot 6H_2O + 3(CaSO_4 \cdot 2H_2O) + 19H_2O = \\ = 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O. \quad (7)$$

Long-term operation of concrete structures in the workshop for the production of titanium dioxide by the sulfate method led to their corrosion by acid and sulfate mechanisms [14]. The result of acid corrosion is the conversion of insoluble alkaline components of concrete (lime and calcium carbonate) into more soluble sulfates or the formation of brittle precipitates of acid hydrates. Sulfates, penetrating by diffusion or capillary adsorption into the cement stone, form ettringite and gypsum crystals with expansive properties. The result is a decrease in the strength of the concrete structure, which affects the critical service life.

4. Conclusions

It has been established that during the production of the TiO_2 pigment by the sulfate method, titanium-containing raw materials are decomposed by sulfate acid at high temperature, accompanied by the release of H_2SO_4 vapor, sulfur dioxide SO_2, hydrogen sulfide H_2S and elemental sulfur. Studies have established that sulfate corrosion leads to the formation of sulfur and iron oxides on the concrete surface. Studies have revealed vast areas of the surface covered with crystals of elemental sulfur, the contents of which are confirmed by the results of X-ray microanalysis. The sizes of sulfur crystals in the image range from 12 to 180 µm, the shape corresponds to the rhombic allotropic modification S8. The penetration depth of iron sulfates into the thickness of concrete is about 50 microns. The microstructure of the surface is loose, with signs of corrosion.

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Conflict of interests

The authors declare no conflicts of interest in relation to this article, as well as the published results of the study, including the financial aspects of conducting the study, obtaining and using its results, as well as any non-financial personal relationships.

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The study was performed without financial support.

Data availability

Manuscript has no associated data.

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