

Chemical Resistance of Cement Stone in Organic Acids

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Abstract – The article studies superposition of corrosive effects occurring at agricultural enterprises. When developing a durable building composite, it is necessary to take into account each type of corrosion to prolong resistance of the environment. The influence of long-term exposure of cement stone samples in organic acids (waste products of mycelial fungi) on physicomaterial properties and morphostructural transformations was studied.

Keywords – portland cement; organic acids; filamentous fungi; corrosion; bio-corrosion; agro-industry.

I. INTRODUCTION

There are a lot of studies on the resistance of building composites in aggressive media [1–13]. This problem is relevant for the agricultural sector, since an integral part of its technological process is associated with the formation of organic waste from a favorable environment for microorganisms [14–16].

Due to the constant struggle with biocorrosion agents by implementing sanitary-preventive measures, corrosive effects are superposed: remedial means (regular premises treatment); biocidal agents (when there are visible signs of damage); waste products (with the growth of animals and birds); microorganisms and their metabolic products (spread of damage). It is obvious that each type of impact causes the operational "fatigue" of building materials and has a significant impact on durability of structures. Evaluation of the impact is an important task for developing methods to prolong resistivity and stability of the material and the construction object as a whole.

The main purpose is to establish patterns of destruction of cement stone in the environment that simulates waste products of filamentous fungi. Portland cement was a research object. It is the most widespread binder.

II. METHODS AND MATERIALS

Cement M500 D0 produced by CJSC (Belgorod, Russia, class CEM I 42.5 N) was used. Chemical and mineralogical composition is presented in Tables 1 and 2.

TABLE I. CHEMICAL COMPOSITION OF CEMENT CLINKER

Oxide content, wt. %						
CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	MgO	other
66.4	21.9	5.36	4.26	0.24	0.5	1.5

TABLE II. ESTIMATED MINERALOGICAL COMPOSITION OF CEMENT CLINKER

Minerals, %			
C3S	C2S	C3A	C4AF
60.3	16.8	7.2	13.3

The compositions were prepared using Matest E095. All samples were produced in metal forms, pre-lubricated with a thin layer of engine oil. Cubic specimens with an edge size of 20 mm were molded (the water-cement ratio was 0.3).

Portland cement samples were placed in the bath with a hydraulic shutter for one day, disintegrated and continued to harden for 27 days. Then some samples were tested using a PGM-100 hydraulic press, the remaining samples were placed in the model environments:

- distilled water (control environment). The water temperature was 19–20 °C. This series of samples was evaluated as a control composition (pH = 6.8);
- aqueous solution of organic acids (the model environment which is the main metabolic products of filamentous fungi (pH = 3.05) [17]) composed of oxalic acid (49%), acetic acid (16%), and citric acid (35%).

The samples were placed in glass desiccators with a tight lid. They were arranged in such a way that all faces of the cube

were in contact with the test environment; polyethylene was placed between the samples (Fig. 1). During the experiment, the desiccators were kept closed and opened once a month for sampling and updating the model environment.

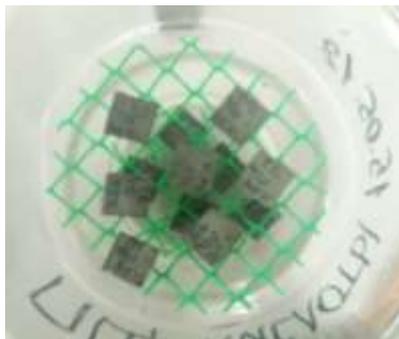


Fig. 1. The system of laboratory exposure of samples in model environments.

The testing was parallel in all the model environments and lasted for 6 months with sampling for control: pH of the curing environment; appearance, weight change, compressive strength, chemical resistance of samples, microstructural and phase transformations of cement stone. The change in mass of the sample cubes was estimated by formula (Eq. 1):

$$G = \frac{(m_2 - m_1)}{m_1} \times 100 \% \quad (1)$$

where m_1 and m_2 are the masses of samples before and after testing.

The pH of the aqueous solutions was determined using an OYSTER-16 pH meter. The measurement was carried out before immersing the samples and after each month of exposure. During the experiment, the desiccator lid was tightly closed and opened once a month.

The coefficient of chemical resistance was calculated by formula (Eq. 2):

$$K_{x.c.} = \frac{R_\tau}{R_0} \quad (2)$$

where R is the average strength of samples exposed in the model environment;

R_0 is the average strength of specimens exposed in water.

The analysis of microstructural changes was carried out monthly using a TESCAN MIRA 3 LMU microscope. Studies of the microstructure of all compositions were carried out by analyzing a representative sample of images by scanning the entire surface of the sample at magnifications of 200 to 50,000. The description was made when shooting. Typical morphostructure areas were surveyed at magnifications of 350; 5,000; 15,000; 36,000.

The phase composition of the initial and exposed to aggressive media samples was assessed using an ARL X'TRA X-ray diffractometer. The shooting conditions were as follows: $\text{CuK}\alpha$ radiation, diffraction angle interval $2\theta = 4^\circ\text{-}64^\circ$, scan step 0.02° , pulse set time - 1.2 sec.

III. RESULTS

When exposing samples in the model environment, significant visual differences were observed. During the first two months, white flocculent neoplasms of the loose structure and small crystalline particles dominated on the sample surface and in the model environment. They settled over the entire surface of the samples and at the bottom of the desiccator. By the 3rd month of exposure, these neoplasms changed color from yellow to brown and covered the samples with an increasingly dense layer without penetrating deep into them.

These phenomena were confirmed by data on the change in the mass of the samples (Fig. 2). There is an increase in the mass of the samples during the first three months. During this period, the surface layer of a new crystalline substance was formed. Subsequent exposure causes leaching of the main products of interaction which is confirmed by a decrease in the mass of the samples.

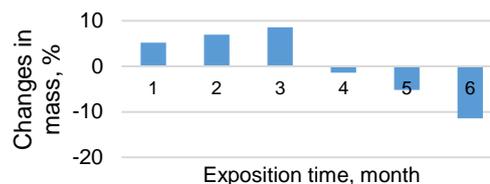


Fig. 2. Changes in the mass of samples of Portland cement held in the organic acids depending on the exposure time.

At the initial stages (up to 1 month), the pH of the environment increases due to the removal of calcium to the material surface and the solution (Fig. 3). It is due to interaction of the mineral components of a Portland cement stone and organic acids. It is known that when samples of a portland cement stone are immersed in water, calcium hydroxide can be released to the surface which means that the compounds can be formed on the surface due to its reaction with acids. During interaction with oxalic acid, calcium oxalates which are insoluble in water are formed. This causes the formation of a temporary protective layer ensuring the stability of the material in acids.

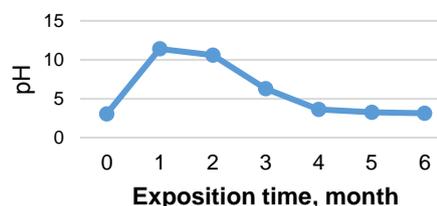


Fig. 3. Changes in Portland cement sample pH held in organic acids depending on the exposure time.

Calcium citrate formed as a result of interaction with citric acid is slightly soluble in water. However, it dissolves in weakly dilute acids, i.e. the process of “reverse solubility” occurs. Adhesion of crystallized salts is much lower compared to calcite formed as a result of carbonization on the surface and in

the cement stone. Acetic acid does not form persistent insoluble compounds (salts), therefore it is the most aggressive.

The effect of the extract on strength characteristics of portland cement stone samples in acids does not have a clear dependence: a rise and a drop in strength were observed (Fig. 4). This is due to crystallization and dissolution.

After the first month, there is a 10% increase in strength compared with samples kept in tap water (Fig. 4) which is due to the formation of insoluble oxalic acid salts and slightly soluble citric acid salts, as well as an increase in the weight of the samples.

There is a decrease in strength by 18% compared with samples aged for 1 month in acids and by 10% compared with samples aged in pure water. It is due to the release of calcium citrate into the solution and exposure to the acetic acid.

In addition, due to high humidity and the lack of forced tightness of containers, natural carbonation of samples occurs with the formation of insoluble carbonate compounds (calcite) which clog the pores and voids and increase its density. Despite the decrease in the compressive strength after 2, 4 and 6 months, its actual value is not less than the grade strength value.

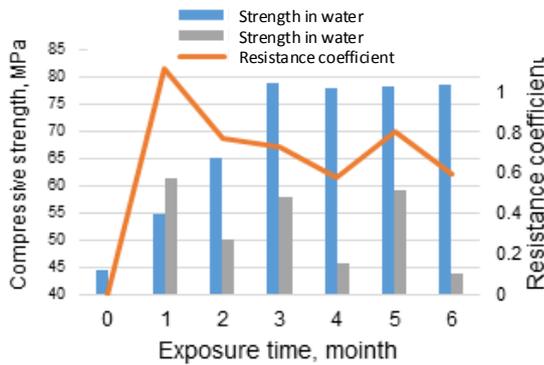


Fig. 4. Changes in the compressive strength and the coefficient of resistance of Portland cement stone samples held in distilled water and organic acids depending on the exposure time.

Exposure of the cement stone in the acid solution causes the formation of a dense mass (Fig. 5, a) consisting of prismatic crystals with characteristic cleavage structures and elongated crystals tightly fused with the main globular mass (Fig. 5, b).

Similar accumulations are observed when exposed for 2 months (Fig. 5, c).

An increase in the duration of exposure to acids with a constant updating of the solution and intensive dissolution of CaO causes the formation of cavities (Fig. 5, d) in which new formations are formed. There are isometric pores with a diameter of up to 100 microns. They are filled with large idiomorphic prismatic crystals growing from the periphery to the center (Fig. 5, f). The edges of the pores are overgrown with smaller tumors which are a mixture of needle-like crystals (not exceeding 5 microns in length) with a globular mass.

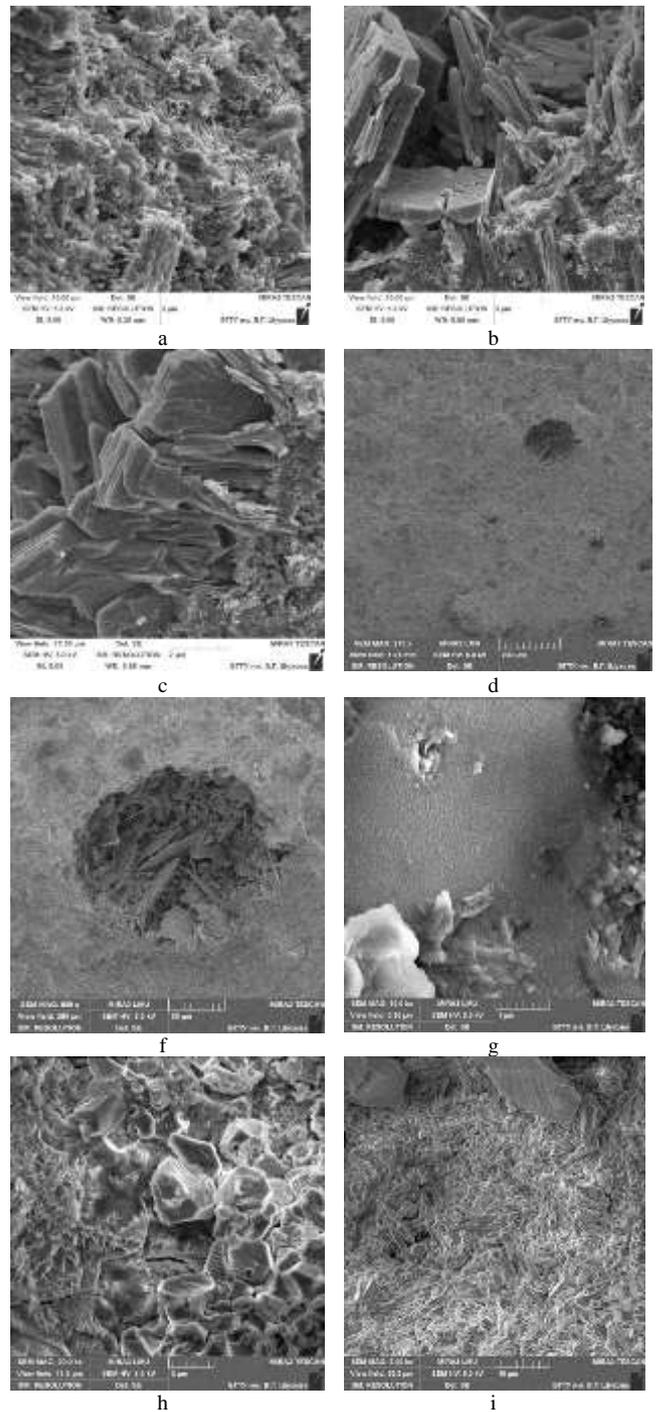


Fig. 5. The microstructure of samples of Portland cement held in organic acids.

In contrast to the control samples of portland cement stone, dissolution structures were observed in the samples after exposure to the acid solution (Fig. 5, g). These are either rather large (up to 20–30 μm) particles with fuzzy edges and irregularly shaped furrows on the faces, or a diffuse globular mass. There are areas of accumulation of new particles up to 2-3 microns in size with blurred edges (Fig. 5, h). They cover the entire bulk of the samples (Fig. 5, i).

A decrease in the total CaO content in portlandite and calcite in samples held for 1 month (Table 3, Fig. 6) by 4.4% (41 wt.%) may be due to the intensification of crystallization of hydrosilicates of the second generation, and formation of insoluble calcium compounds when interacting with oxalic acid.

TABLE III. MINERAL COMPOSITION OF A PORTLAND-CEMENT STONE EXPONED IN THE SOLUTION OF ORGANIC ACIDS, MASS %

Mineral	Duration of hardening, months						
	28 days	1	2	3	4	5	6
Alite	18.92	11.1	11.9	13.5	13.8	16.1	10.1
Belite	18.87	16.7	16.4	16.5	18.1	20.0	15.6
Brownmillerite	13.21	3.1	2.8	5.1	4.3	5	2.5
Portlandite	4.29	17.4	22.3	23.4	23.3	27.0	13.0
Calcite	24.70	43.9	37.5	32.2	32.6	28.6	54.9
Aragonite	18.36	-	-	-	-	-	-
Waterite	1.65	-	-	-	-	-	-
Ettringite	-	7.8	9.1	9.3	7.9	3.3	3.9

The maximum decrease in the total content of CaO in Portlandite and calcite to 36 mass. % (by 8.9% of the control composition of cement stone, aged in water) occurs during the four-month exposure.

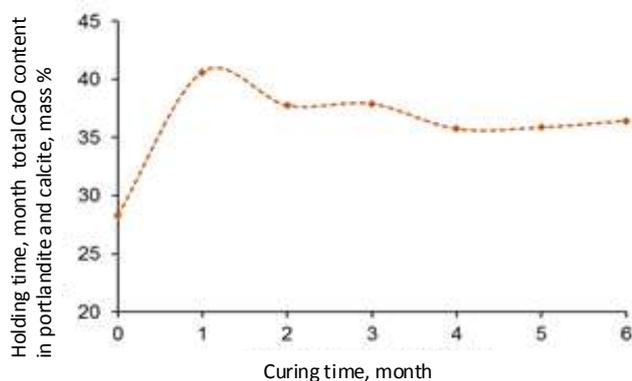


Fig. 6. The dependence of the CaO content in portlandite and calcite on the exposure time for samples of portland cement stone held in organic acids.

Minor changes (increase) in the total CaO content in Portlandite and calcite after 4 months of exposure to acids are in the experimental error area or may be caused by recrystallization of calcium hydrosilicates in the presence of acids. However, these minor changes cannot be identified by XRD analysis of this polymineral system.

IV. CONCLUSION

Thus, the waste products of filamentous fungi contribute to the consistent dissolution of soluble alkalis, crystallization of tumors, as well as reduction of the amount of readily soluble compounds. When the solution is updated (monthly) and the pH is lowered, hydration products can be recrystallized which decreases the strength as a result of intensive leaching and formation of soluble unstable calcium compounds. This ensures additional porosity of the composite reflected in a decrease in the mass of the samples.

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