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Strength and structure of cement stone exposed to domestic chicken coop

V Stroková¹, V Nelyubova, M Rykunova, U Dukhanina

Department of Materials Science and Technology of Materials, *Belgorod State Technological University named after V G Shukhov*, 46 Kostyukova Street, Belgorod, 308012, Russian Federation

¹E-mail: vvstrokova@gmail.com

Abstract. The paper deals with two types of corrosion at the enterprises of the agro-industrial complex: chemical (induced by periodic measures for premises sanitization) and biological (through favorable for the metabolism of microorganisms environment). There are the results of full-scale tests of cement stone in the conditions of a domestic chicken coop without taking measures to clean and disinfect the premises during the period of 11 months. The authors showed changes in the microstructural features of the cement stone and strength characteristics, depending on the area of operation (I – aerial; II – floor with hay and wood chips; III – poultry excrements). On the surface of the samples kept in each zone, the growth of mycelium was not detected. Zone III had the greatest negative effect on strength characteristics of cement stone, particularly 10 % decrease in strength compared to the control, while the microstructure of samples had no new formations of second generation and the presence of dissolution structures. The increase in strength by 25 % in zone II with respect to zone III is explained by the presence of a wet litter contributing to the calmatation of the cement pores and the filling of microcracks in matrix structure. It was found that the smallest external and strength changes were in cement samples exposed in the zone I.

1. Introduction

Control of microbiological corrosion is an important factor for ensuring environmental safety and operational reliability of buildings and structures [1–3]. In agro-industrial complex degradation of construction materials of and its structures is particularly acute due to specific environmental conditions [4, 5]. Corrosive effect on materials is primarily brought by microorganisms (excrement, flush water, feed waste, organic acids, mineral compounds, carbon dioxide, hydrogen sulphide and ammonia, etc.), and disinfectants used for sanitary and hygienic treatment (caustic soda, formalin, lime chloride, neutral calcium hypochloride, glutaric aldehyde, iodine monochloride, freshly slaked lime, soda ash, agents based on peroxyacetic acid, hydrogen peroxide, etc.) [6,7]. Unfortunately, the existing standards for assessing building materials' resistance to fungi do not include estimation of phase, morphology and structure transformations in degraded materials, which directly determine the durability of the entire material under biological effects. Meanwhile, empirical methods considering physico-mechanical and phase-structural properties of materials under simulated or natural conditions



are highly effective to assess biological stability of construction composites [8–12]. At the same time, all methods and research techniques should be standardized and designed to specific operation of a particular material and related to physical, chemical, biological or their superposition (complex effects) of a material [13–19]. Depending on the research purposes we should monitor the type of aggressive effect, environment composition, material degradation, which influence operational characteristics of the material.

Despite difficulty in monitoring materials parameters in natural environment, it is an effective mean to assess the dynamics of structure formation processes with a minimum error and assumptions. Although forced disinfection of premises has benefits as almost complete destruction of pathogenic microflora, there are still disadvantages as frequent surface treatment of structural elements of buildings and structures with remediation substances. Therefore, disinfection mostly leads to material gradual destruction under the action of aggressive acids and electrolytes.

In this regard, the main purpose of this work was to study the effect of the cement composites operation environment on their degradation (change in the physicomechanical characteristics over time) under the natural, full-scale conditions of a domestic poultry farm.

2. Materials and methods

In our work we used cement M500 D0 grade cement produced by CJSC (Belgorod, Russia, class CEM I 42.5 N). Chemical and mineralogical composition is presented in table 1 and table 2, respectively.

Table 1. 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 2. Estimated mineralogical composition of cement clinker

Minerals, %			
C3S	C2S	C3A	C4AF
60.3	16.8	7.2	13.3

Cement was manually mixed with distilled water (pH=7.2) prior to be put in metal forms with size 4×4×16 cm (water-cement ratio was selected according to the normal cement density and was 0.3). After molding the samples were hardened for a day in a bathtub with a hydraulic seal in molds, then unmolded and continued hardening for 27 days. After hardening for 28 days the samples of obtained cement stone we assessed the effect of the operating conditions on strength and microstructural characteristics of cement stone.

To cause biocorrosion we simulated the conditions close to real operation poultry farm (domestic hens breed Loman Brown in the amount of 20 hens and 1 rooster). Poultry farm s are distinguished by highly aggressive environment, due to the high content of nitrogenous and phosphorous compounds released in the process of bird vital activity. We exposed cement stone for 11 months (January–November, 2017). During the experiment cleaning and treatment of the premises with disinfectants was not carried out. Premises of the domestic chicken coop was a covered building of concrete blocks, the roof covering is made of asbestos cement shingle, the room has a hole in the wall, measuring 40×40 cm, located in the lower part of the wall for birds free-range. The walls of the chicken coop had no a finishing layer and additional thermal insulation without heating. The area of the room was 15 m². The domestic chicken coop was located in the private sector in the town of Stroitel, Belgorod Region. The climate of the Belgorod region is characterized by frequent snowfalls in the winter period (November – February), the maximum sub-zero air temperature was –30 °C, thaws begin in April and were characterized by frequent precipitations, in summer the maximum temperature was +35 °C.

In experiment the samples were placed in three zones of a domestic poultry farm related to different corrosive impact: I – aerial zone (samples did not interact with birds metabolic by-products); II – floor zone covered with hay and wood chips (birds had access, but rarely were in this area); III – aggressive zone (maximum accumulation of birds excrement). The control sample were 4×4×16 beam samples from the same batch that were stored during this period under laboratory conditions with a constant temperature $t = 22\text{ }^{\circ}\text{C}$.

As criteria for assessing the degree of influence of aggressive components of the environment on cement materials and their comparison with control samples we have considered microstructure, appearance, and strength characteristics of the samples. In order to determine the depth of degradation in material bulk, all samples were preliminary sawn into plates from the outer surface to the centre with 0.5 cm interval (figure 1). For the studies, plates were selected under the numbers from 1 (closest to exposure zone) to 4 (closest to bulk).



Figure 1. Cut plates of exposed cement sample

Scanning electron microscopy was used to study the microstructural features of the samples using a scanning electron microscope TESCAN MIRA 3 LMU (SEM, Czech Republic) in high vacuum mode (InBeam) using a Schottky cathode of high brightness. The study of the microstructure of all compositions was carried out by analyzing three samples of plates of each type, by scanning the entire surface of the sample at magnifications from 200 to 50,000 times, with a direct description when shooting. For the subsequent demonstration of the research results, photographs of sites of morphostructure typical for all samples were taken at identical magnifications: 350; 5,000; 15,000; 36,000 times.

External changes in the surface of the samples, the presence / absence of sporulation and hypha of filamentous fungi were studied by means of microbiological microscope AXIO SCOPE A1.

To estimate material strength, we measured ultimate compression strength, MPa by means of the hydraulic press PGM-100 MG4 (Chelyabinsk, Russia) under speed of loading 0.1 MPa/s.

3. Results and discussion

It has been revealed that the least external changes of surface characteristics were in cement samples exposed to the aerial zone since there is no obvious surface damage (figure 2a). Becoming more aggressive environment causes a change of specimens color: we see an obvious zoned pigmentation and the formation of efflorescence's on their surface (figure 2b and 2c). Nevertheless, analysis by microbiological microscope demonstrates no obvious signs of a mycelium. This is due to a number of factors: first of all, cement has initial high alkalinity. Secondly, there is a rather high degree of pollution of samples in zones II and III. Layer of dirt stick to the surface of sample and block macropores which leads to some "protection" of the sample surface. Thirdly domestic poultry farming, as a rule, is characterized by a small number of livestock. This significantly increases the time required for the development of microflora – biocorrosion agents. Among other things, it explains the absence of visible damage on the surface of samples held in zone I (air) of the coop: no direct contact with the poultry and products of its vital activity occurred, and the small number of birds does not provide the proper conditions for the development of degradation processes.

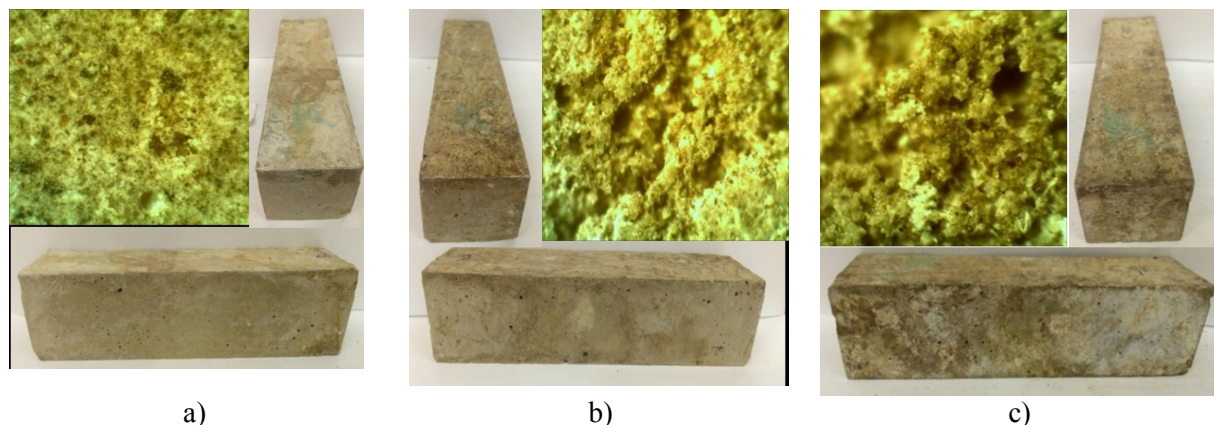


Figure 2. Optical image and appearance of cement exposed to domestic chicken coop in aerial (a), floor (b), and aggressive (c) zones (magnification \times 60)

Analysis of strength characteristics confirms the results of visual analysis. Exposure in coop' aerial environment does not significantly affect the value of compression strength (50 MPa) compared to the control – 49 MPa (figure 3, control and I zones). In floor zone cement stone has a 20 % increase in strength (figure 3, II zone) mostly explained by the formation of conditions for the gradual completion of the hydration processes of the cement stone with constant moisture access to the material. Decrease in strength of cement kept in aggressive zone (figure 3, aggressive zone) (by 25 % compared to floor zone (figure 3, III) is primarily due to the influence of nitrogenous and phosphorous compounds in the poultry litter that exert a sharp corrosive effect. This results in splitting of silicate compounds in the structure of the material with the formation of readily soluble compounds washed out both from of the volume of material and its surface.

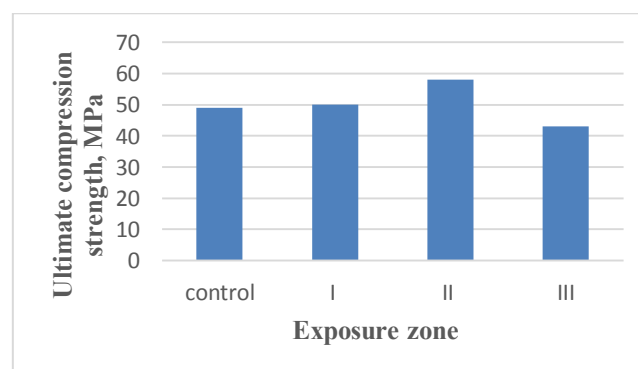


Figure 3. Compression strength of control cement and of cement exposed to different zones.

When studying the morphostructural features of the selected plates, firstly, general view of all the samples was analyzed with a magnification of 300...350 times. This was done to determine the degree of crack formation during sample preparation, macroporosity of the total mass, morphology of the pores. A visual assessment of plates showed that in the various holding zones in all samples the air-entrapped sections were identified, which are identified by a near-isometric pore morphology (figures 4a and 6e) with size diapason 13...20 μm . This technological pores act as dampers inhibiting the development of microcracks in the volume of the material. Meanwhile, they are also easily filled with corrosive acid in case of keeping the samples in conditions favorable for growth and development of microorganisms, which leads to faster corrosion of the cement.

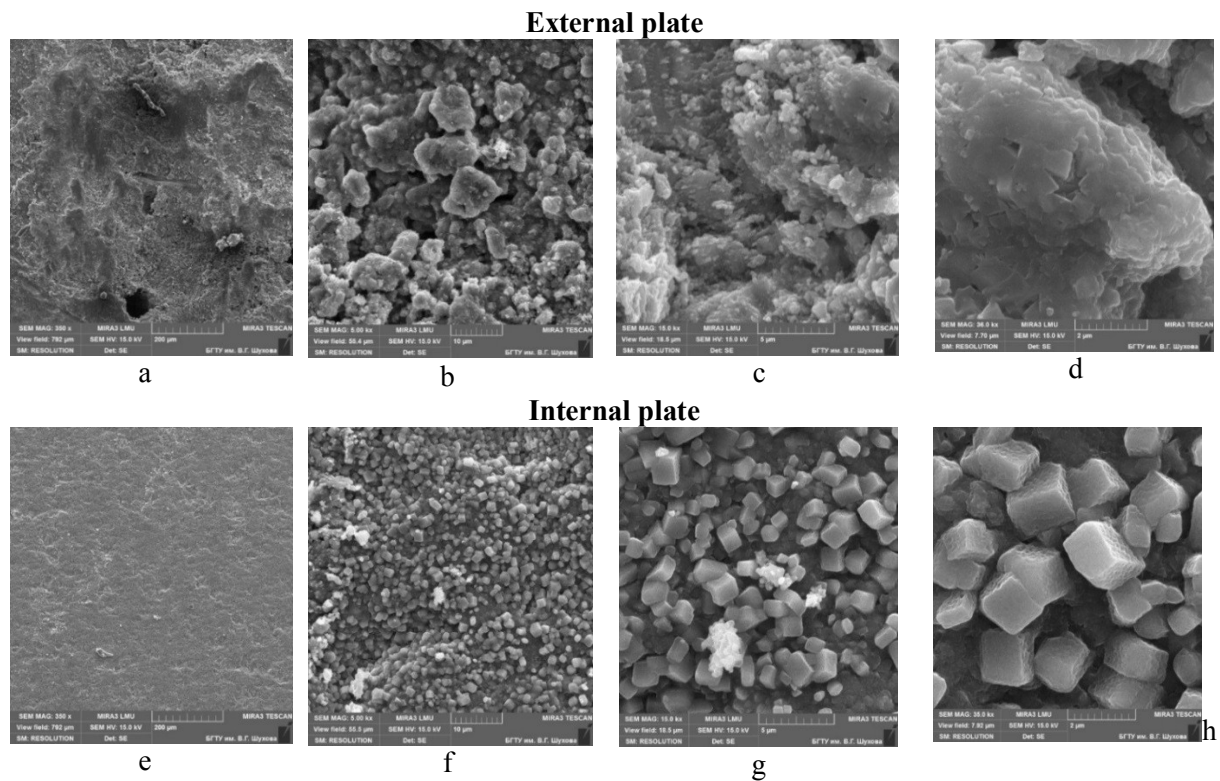


Figure 4. Microstructure of the sample from zone I at different magnification: *a, e* – 350 times; *b, f* – 5,000 times; *c, g* – 15,000 times; *d, h* – 36,000 times.

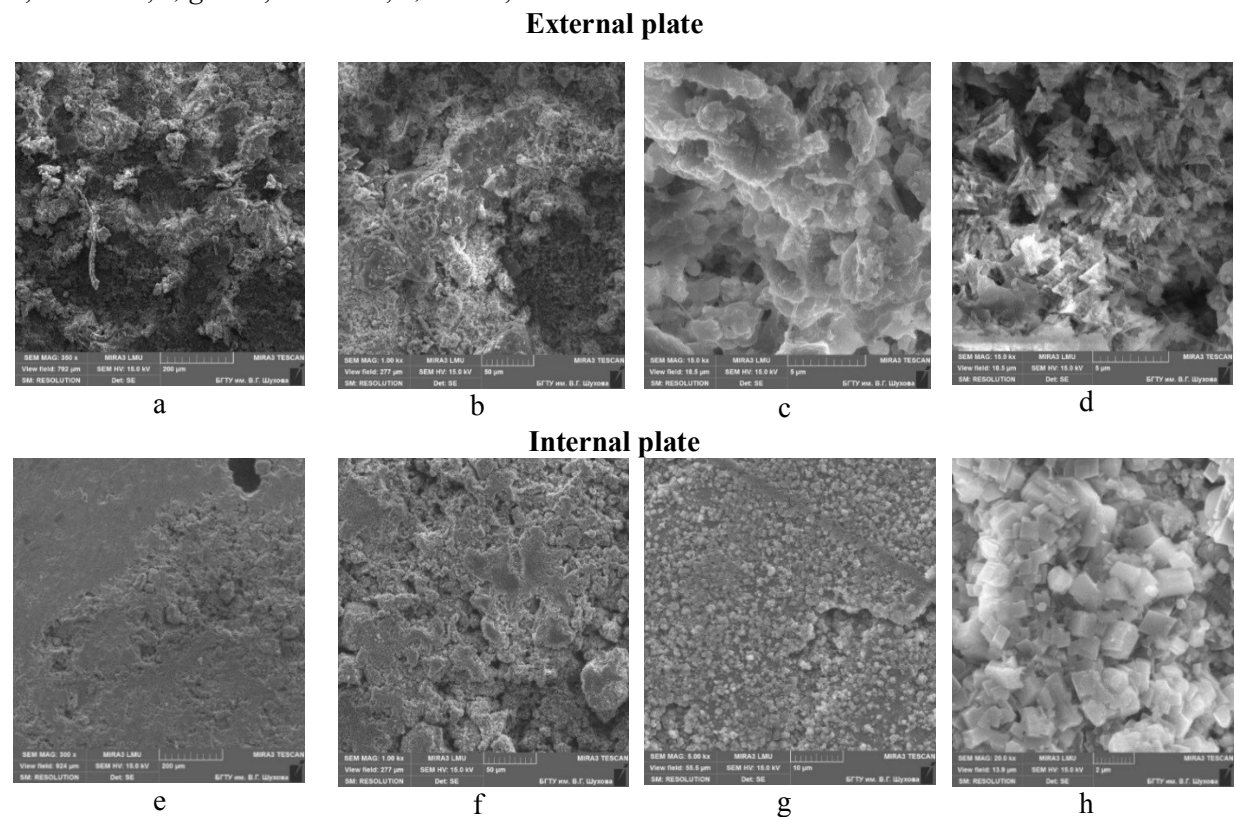


Figure 5. Microstructure of the sample from zone II at different magnification: *a, e* – 350 times; *b, f* – 5,000 times; *c, g* – 15,000 times; *d, h* – 36,000 times.

Due to high humidity, in all three zones stone structure has minimal deformations and no complete destruction (figures 4a, 4e, 5a, 5e, 6a and 6e). The net arrangement of cracks with an opening width up to 1 nm indicate a plastic character of the material structure associated with a high water content in the micro- and capillary space of the hardening system. This, in turn, leads to the continuation of hydration processes during the operational period.

The internal parts of all types of plates are distinguished by a more monolithic structure (figures 4e, 5e and 6e), compared to the external that were directly in contact with the external environment. Also the structures of the saw cuts are seen (figure 4a, 5a and 6a) – mechanical damages when cutting specimens.

The morphology of individual structural elements is quite identified (figures 4b, 5b and 6b). On external plates of all samples we observe structural damage of decompressed zones (figures 4b, 6b, 4c and 6c) and agglomerates from the products of hydration with the size of 10...50 μm . This can be explained by the maximum destructive processes in the upper layers of the material because of the contact with aggressive environment. In the samples held in the air and on the floor in the wood chips with the free air access we see new formations of second generation as crystals with a clearly defined face of 0.4...2 μm in size, i.e. growth patterns (figures 5c, 5d, 6c and 6d). These can be trigonal crystals of calcite. On microphotographs, crystals of trigonal syngony look like rhombohedra up to 1 μm in size (figure 6d).

Morphology of the structural elements of the inner part of the plate (figures 4f, 5f and 6f) has difference depending on the sample holding area.

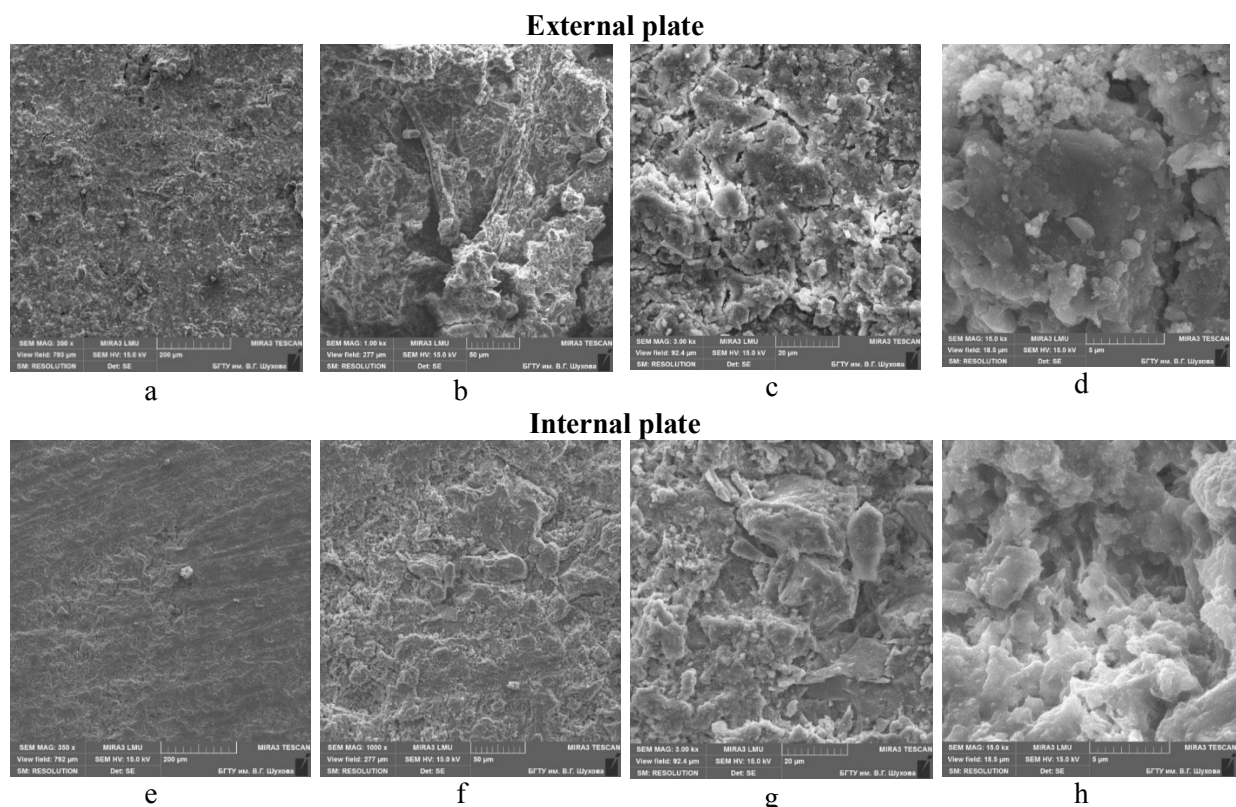


Figure 6. Microstructure of the sample from zone III at different magnification: a, e – 350 times; b, f – 5,000 times; c, g – 15,000 times; d, h – 36,000 times.

Samples kept on air has a plenty of new formations of the second generation. These are rhombic aragonite crystals, identifiable starting 5,000 times zooming (figures 4f, 4g). The size of new formations reaches 1–2 microns. Large enough and idiomorphic crystals of carbonates of such a

polymorphic modification (figure 4h) could be formed with a sufficient amount of portlandite in the material layer, and a free uniform flow of CO₂ into the volume of the material. Similar formations are also identified in samples kept in zone II (figures 5g, 5h), i.e. in conditions of free access to the samples of both moisture and air.

Samples that were kept in the most bioaggressive and moist environment – zone III are distinguished by the absence of idiomorphic crystals of new formations (figure 6c, 6d, 6g, 6h). Samples from that zone are characterized by the structures of dissolution, the absence of clear crystal morphology boundaries.

It can be said that the zone III is characterized by the maximum degree of corrosion, the absence of visible growth structures, faceted new formations, the presence of dissolution structures. In zones I and II the characteristic habit of the crystals is observed that confirm the presence of carbonates of two polymorphic modifications – calcite (trigonal syngony) and aragonite (rhombic system). The reason for the formation of different polymorphs, as well as the change in the concentration of each of the minerals at a distance from the periphery to the center of the samples cannot be definitely indicated, but this is not the goal of the present studies.

4. Conclusion

The greatest degree of impact has the environment of the floor where the samples were kept in excrements: the loss of strength is more than 10 %, the microstructure of the samples is characterized by the absence of new formations of second generation, which is caused by the presence of aggressive acids in the poultry manure. Storage of materials in a humid environment without obvious effects of waste from poultry leads to a 25 % increase in strength, which is also confirmed by colmatation of pores and cracks in the structure of the material. This is ensured by a more complete flow of hydration processes of cement in the long term.

Thus, it is shown that the rate of corrosion processes is determined by the characteristics of the corrosive environment, the reactivity and permeability of concrete, and the degree of its damage directly depends on the amount of microorganism vital activity products that are released into its volume and the amounts of corrosion products leached from concrete. Based on the foregoing, in order to maintain a safe regime for the management of animals and birds and the effective functioning of the "disinfectant - material" system, it is necessary to design agricultural premises using building materials with prolonged fungicidal and algicidal properties, which will increase the intersanation time; to switch to a new purification system by using more sparing chemicals; neutralize generation of mycotoxicosis in the initial stages of evolution; avoid contamination of premises with microorganisms, reduce the biological fatigue of the premises and, as a consequence, reduce the destructive effect of the products of their metabolism.

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