Materials Science Forum
ISSN: 1662-9752, Vol. 945, pp 269-275
doi:10.4028/www.scientific.net/MSF.945.269

Submitted: 2018-10-19
Accepted: 2018-10-22
Online: 2019-02-06

Structural Transformations of Cement Stone in Conditions of Development of the Biocenosis of a Poultry Enterprise

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Keywords: Cement stone, aggressive environment, biocorrosion, phase-structural analysis, stock breeding complex.

Abstract. The results of the investigation of phase-structural transformations of cement stone as a result of the influence of the aggressive environment of the poultry farm are presented. Analysis of the change in the phase composition of cement stone samples showed that according to the average content of C3S increase in the increase of degree of hydration is represented by the sequence: zone I (air medium with minimal aggression) - zone III (wet environment with maximum concentration of active substances) - zone II (air zone with periodic aggressive action). The degree of carbonization, depending on the test conditions of the samples, is characterized by a similar zonal dependence. In this case, the removal of CaO during the acid leaching of the peripheral regions of the samples was detected to a greater extent during testing in zones II and III.

Introduction

All over the world researchers pay great attention to the corrosion resistance and durability of building composites [1-20]. It is known that the corrosion resistance of concrete depends on the permeability of the cement stone for liquid and gaseous agents, as well as its reactivity when exposed to them. This means that the service life of the composite depends on the differential porosity and phase composition of the cement stone. It is obvious that in the case of enterprises of the agro-industrial complex, the problem of structural degradation is particularly acute, since in this case there is a superposition of types of influence: on the one hand living organisms of different species function on surface and in the volume of the composite and on the other - to ensure sanitary-hygienic standards, sanation (treatment) of premises is required to reduce the concentration (or complete suppression) of the pathogenic microflora.

It is known that frequent treatment of buildings structures surfaces and structures with sanation substances leads to their gradual degradation due to destruction under the action of corrosive acids, the outwashing of soluble substances and as a result - the formation of additional porosity of materials, microcracks, etc.

Thus, it is not possible to give an adequate assessment of the contribution of biocorrosion with the analysis of concrete samples used in actual production conditions, in view of periodic preventive measures and forced disinfection with caustic disinfectants.

The purpose of this work is to study the structural changes in cement stone, exploited in various areas of the poultry farm: with direct contact with animal metabolic by-products, as well as in areas with minimal contact, distinguished by a high degree of concentration of corrosion agents in the air.

Materials and Methods

In this work to assess the phase-structural transformations of cement stone happening in the material under the action of biocorrosion, the beam samples were placed in three zones of a domestic poultry farm, taking into account the gradation of the impact of the corrosive environment. For this purpose, the following zones were identified: I - aerial: the samples were exhibited as high as possible, but they did not contact the birds metabolic by-products; II - floor with hay and wood chips: samples were on the floor, birds had access, but rarely were in this area; III - aggressive: the zone with the maximum accumulation of excrement of birds and their constant renewal.

The choice of poultry farm environment for assessing structural fatigue as a result of biological exposure is due to the fact that poultry farms are distinguished by the most aggressive formed environment, due to the high content of nitrogenous and phosphorous compounds released in the process of vital activity of the bird, which exert an extreme corrosive degradation effect on cementitious materials

Full-scale trial continued for 11 months (January-November 2017). During the experiment cleaning and treatment of the premises with disinfectants was not carried out.

As a binder M500 D0 grade cement produced by CJSC Belgorod cement were used. Preparation of the sample compositions was carried out manually, the samples were made in metal forms 4×4×16 cm, the water-cement ratio was selected according to the normal cement density and was 0,3, after molding the samples were hardened for 1 day in a bathtub with a hydraulic seal in molds, then unmolded and continued hardening for 27 days. The absence of aggregate in the composition is due to the need to minimize the effect of quartz reflections in identifying changes occurring in the phase composition during X-ray phase studies. After hardening for 28 days the samples of the cement stone under investigation were placed in three zones of a household poultry farm.

To study the quantitative phase composition of the newly formed and recrystallized substance in cement stone, all beam samples were sawn after the exploitation in the poultry farm into plates from the outer surface to the center with 0,5 cm interval. For the studies, plates were selected under the numbers: 1 - the most extreme plate, directly in contact with an aggressive environment, 4 - the closest to the center of the sample beam.

The X-ray diffraction was obtained using an X-ray diffractometer ARL X`TRA using β-filtered Cu-anode radiation. The interval of the Bragg angles of photography is 4°-64°, the scanning step is 0,02°. To identify crystalline phases, a PDF-2 diffraction database was used with application of the Crystallographica Search-Match v.2.0 search shell.

The quantitative XRF of the samples was carried out in a full-profile version using the program DDM v.1.95 e. As structural models of the crystalline phases of cement stone, identified on the basis of the PDF-2 diffraction base, the ICSD structural base data was used. Here are the structural models that were used in the calculations: C3S (triclinic modification) - 4331-ICSD, β-C2S - 81096-ICSD, C3A - 1841-ICSD, C4AF - 2841-ICSD, trigonal quartz - 16331-ICSD, portlandite - 202233-ICSD, gypsum (calcium sulfate dihydrate) - 27221-ICSD, calcite - 16710-ICSD, aragonite - 15198-ICSD and ettringite - 90823-ICSD.

The weight contents of CaO in Ca(OH)2 and CaCO3 were calculated by subtracting components from their weight concentrations - H2O for portlandite and CO2 for calcium carbonate by Eq. 1:

$$C_{CaO}^{Ca(OH)_2} = \frac{c_{Ca(OH)_2}\cdot(\nu_{Ca(OH)_2} - \nu_{H_2O})}{\nu_{Ca(OH)_2}} \quad \text{and} \quad C_{CaO}^{CaCO_3} = \frac{c_{CaCO_3}\cdot(\nu_{CaCO_3} - \nu_{CO_2})}{\nu_{CaCO_3}}, \qquad (1)$$

Where $C_{CaO}^{Ca(OH)_2}$ and $C_{CaO}^{CaCO_3}$ – weight concentrations of CaO in portlandite and calcium carbonates, $C_{Ca(OH)_2}$ and C_{CaCO_3} – concentration of portlandite and calcium carbonate in cement stone, and $\nu_{Ca(OH)_2}$, ν_{CaCO_3}, ν_{H_2O} and ν_{CO_2} – molecular weights of the indicated components.

The relative content of CaO in portlandite from the amount of CaO in Portlandite + calcium carbonates was found using Eq. 2:

$$\frac{C_{CaO}^{Ca(OH)_2}}{C_{CaO}^{Ca(OH)_2} + C_{CaO}^{CaCO_3}}, \qquad (2)$$

Results

As follows from the results of the quantitative XRF (Fig. 1), only the reflections of crystalline inorganic phases - typical components of cement stone - are found on X-ray diffraction patterns. At the same time, there are no mineral formations that are the result of the interaction of corrosive-aggressive organics (metabolic products) with minerals of cement stone.

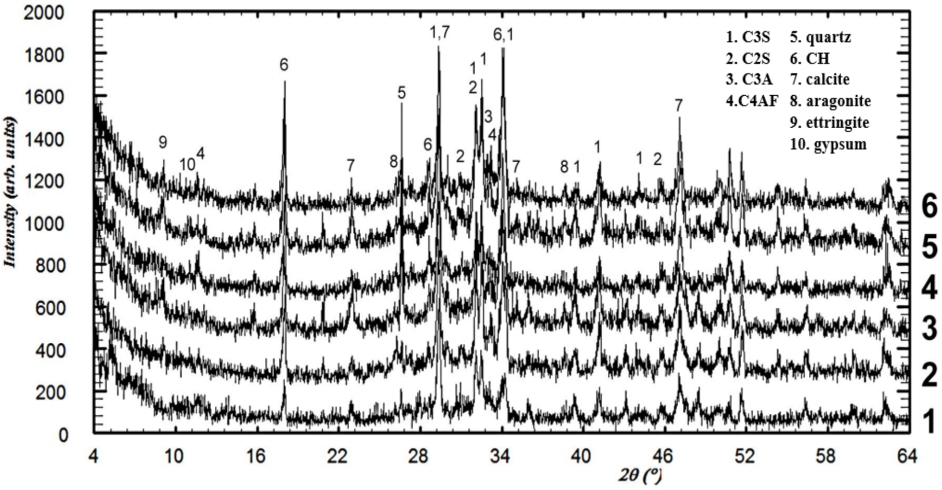

Fig. 1. Qualitative identification of X-ray patterns of cement stone samples: zone I – brink edge (1), centre (2); zone II – brink edge (3), centre (4); zone III – brink edge (5), centre (6)

At the same time, variations in the concentrations of cement stone clinker components and epihydrational formations - portlandite, calcite and aragonite - are noted (Table 1). Therefore, the concentrations of C3S, portlandite and calcium carbonate - calcite and aragonite were chosen as the main indicators of the effect of the corrosive-aggressive environment of various zones of testing of cement stone samples.

Table 1. The quantitative composition of cement stone in dependence from the conditions of exposure

Mineral / compound	Concentration of crystalline components, wt. [%]					
	Zone I		Zone II		Zone III	
	Brink edge	Centre	Brink edge	Centre	Brink edge	Centre
C_3S	25,32	26,39	18,26	17,91	20,97	26,65
β-C_2S	8,56	11,24	9,12	10,27	8,76	11,01
C_3A	2,72	5,97	5,36	5,93	2,46	5,45
C_4AF	16,33	12,8	7,25	9,62	8,89	6,99
Quartz	0,82	0,5	3,35	5,9	1,07	1,16
Portlandite	8,53	13,27	15,06	30,28	19,14	27,04
Gypsum	n/f	n/f	n/f	n/f	1,15	n/f
Calcite	27,49	16,37	27,95	11,21	14,49	11,3
Aragonite	6,5	9,15	4,28	8,89	3,87	6,84
Ettringite	3,73	4,31	9,37	-	18,73	3,56

The degree of hydration of cement stone during hardening in various zones can be estimated from the residual concentration of C_3S. In the average values of the C3S content, a row of hydration activity can be represented by a sequence: zone II → zone III → zone I (Fig. 2).

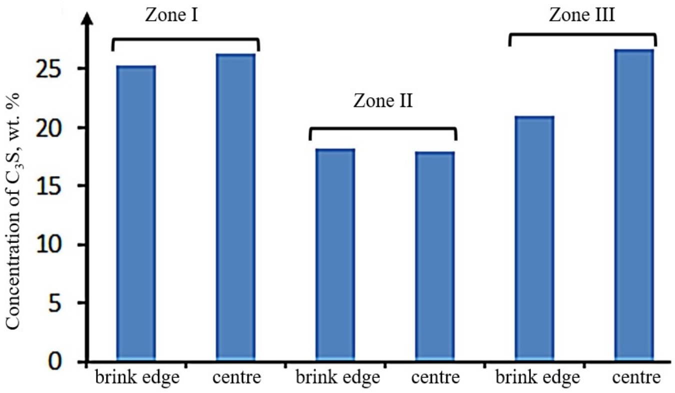

Fig. 2. Distribution of residual C_3S concentration by regions of cement stone samples aged in different zones

At the same time, the content of portlandite (Table 2), as an immediate product of hydration of C3S, demonstrates noticeable variations, both in sample areas and in zones.

A graphic illustration of the relationship «Concentration of C_3S – Concentration of Portlandite» (Fig.3) shows a breakdown of the compositions of cement stone samples from different zones into three disjoint areas. Thus, on the basis of the mentioned above dependence, it can be concluded that the external environment of the zones used in this work has a different effect on the hydration of C_3S.

At the same time, calcium carbonates (Table 1), which are products of carbonation of portlandite, are also subjected to significant concentration variations. Illustration of the dependence «Concentration of C_3S – Concentration of calcium carbonates (calcite + aragonite)» (Fig. 4), as well as the dependencies in Fig. 3 shows the breakdown of the compositions of cement stone samples from different zones into three disjoint areas.

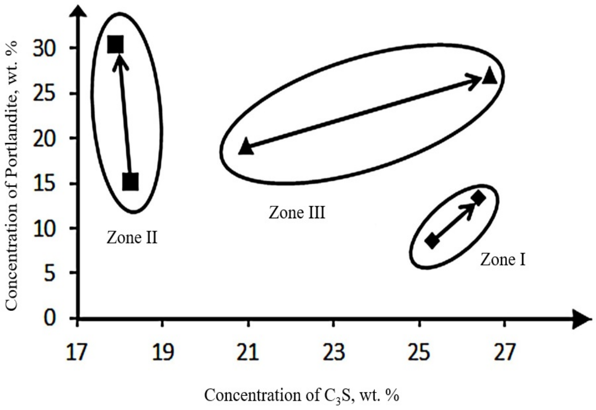

Fig. 3. Graphical illustration of the dependence «Concentration of C_3S – Concentration of Portlandite» with the distribution of samples from various zones (Arrows indicate the direction from the brink edge to the center of the samples)

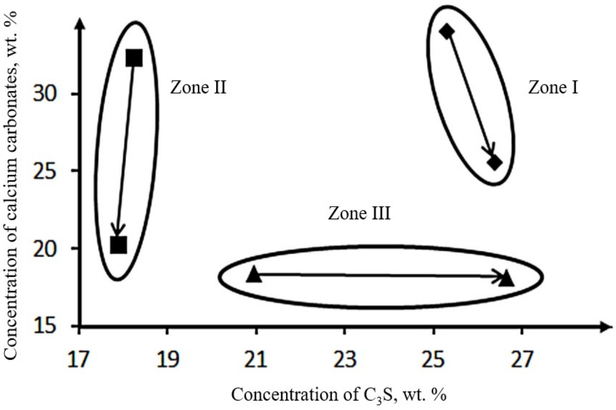

Fig. 4. Graphical illustration of the dependence «Concentration of C_3S – Concentration of calcium carbonates (calcite + aragonite)» with the distribution of samples from various zones

Dependencies on Fig. 3 and Fig. 4 show somewhat different effects of the external conditions of different zones on the concentration values of the products of hydration (portlandite) and carbonization (calcium carbonates). Therefore, in order to correctly estimate the balance of lime in cement stone samples in different impact zones, it is advisable to bring these dependencies to an invariant parameter - the total concentration of lime in portlandite and calcium carbonates.

Performed calculations using Eq. 1 and Eq. 2 (Table 2) made it was possible to demonstrate the distribution of the samples in the coordinates "Concentration of C3S-Concentration of CaO in

Portlandite and Calcium Carbonates" (Fig.5) and to show the averaged dependences illustrated in Fig. 3, Fig. 4.

To determine the dependece of the degree of carbonation of portlandite from regions and aggressive zones, a histogram of the dependence of the parameter Eq.2 from test areas and sample parts was constructed Fig. 6 (Fig. 7).

Table 2. Conversion of the concentrations of calcium-containing components to the content of CaO

Estimate indicators	Concentration of CaO, [%]					
	Zone I		Zone II		Zone III	
	Brink edge	Centre	Brink edge	Brink edge	Centre	Brink edge
Portlandite	6,45	10,04	11,40	22,92	14,49	20,46
Calcium carbonates	29,23	21,94	27,71	17,28	15,79	15,60
$\frac{C_{CaO}^{Ca(OH)_2}}{C_{CaO}^{Ca(OH)_2}+C_{CaO}^{CaCO_3}}$	0,180	0,314	0,291	0,570	0,478	0,567

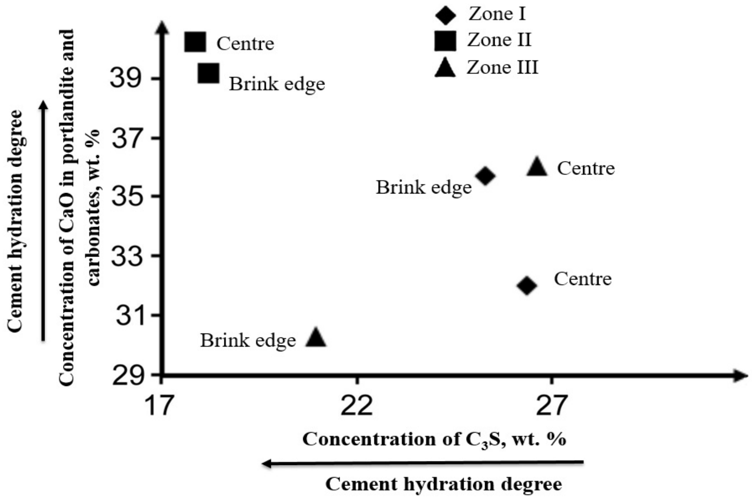

Fig. 5. The total content of CaO as a function of the content of C_3S

If we take as the reference point the value of Eq.2 in the center of the sample, where the carbonization degree is known to be lower than at its periphery (Fig.7), then, as follows from the above distribution, the degree of carbonation of portlandite is higher at the periphery of the samples. On the basis of the above results, it is possible to present the degree of carbonization in the conditions of different samples testing zones in the form of a row of carbonization increase: zone III → zone II → zone I.

Knowing the total content of CaO (in portlandite and calcium carbonates) in different parts of the samples and test areas, it is possible to determine whether calcium was removed from the outer zones of the samples during acid leaching under the conditions of different treating zones (Fig. 8).

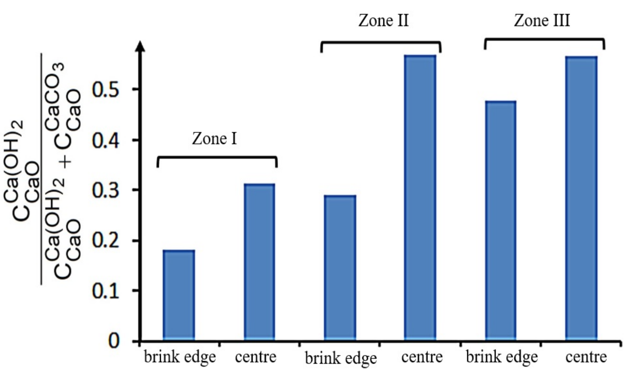

Fig. 6. Distribution of the relative content of CaO in portlandite

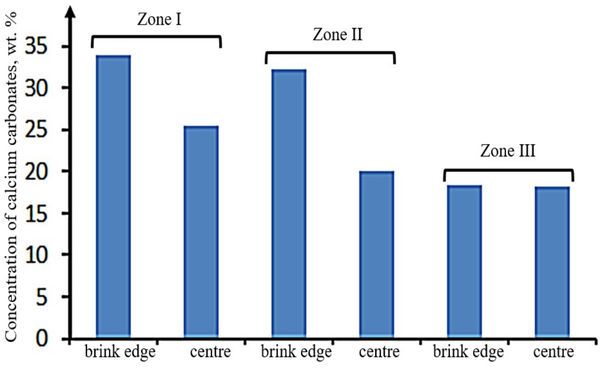

Fig. 7. Distribution of calcium carbonate content

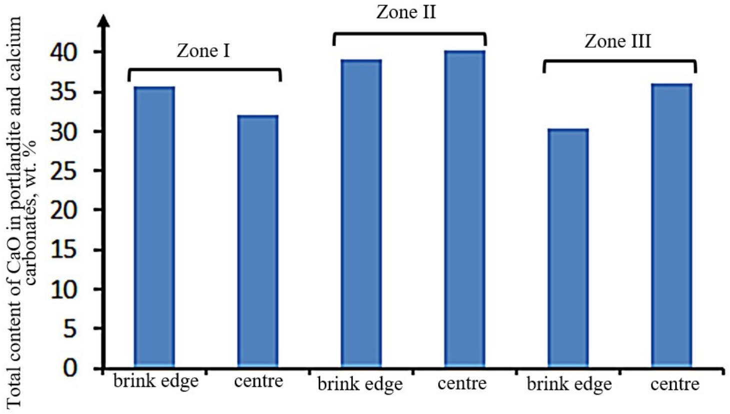

Fig. 8. Balance of CaO by parts of samples and test zones

Summary

Thus, in the test zones II and III, calcium can be removed during acid leaching of cement stone samples (CaO content in the periphery is less than in the center). The reverse trend is observed in the sample from zone I. This anomaly can be interpreted as a result of the diffusion of calcium from the central regions of the sample to the peripheral ones. The explanation of the reasons for this phenomenon is beyond the scope of the task to carry out XRF of cement stone samples after treating in aggressive conditions. In any case, additional studies are needed using methods for determining the total and local elemental compositions.

Thus, in averaged values of C3S content, the series for increasing the degree of hydration is represented by a sequence: zone I → zone III → zone II. The degree of carbonization in conditions of different test zones of samples is characterized by a similar zonal dependence. In this case, the removal of CaO during the acid leaching of the peripheral regions of the samples was detected to a greater extent during testing in zones II and III.

Acknowledgment

The research is made in the framework of State Task of the Russian Federation Ministry of Education and Science № 7.872.2017/4.6. Development of principles for the design of ecologically positive composite materials with prolonged bioresistance. 2017–2019.

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