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Effect of agents of organic origin on concrete degradation

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Abstract. Concrete and structural elements used within agricultural activities are affected by a range of factors, which have a significant effect on properties and durability of concrete. Among typical factors belong corrosive effect of silage juices, excrements of farm animals or also effect of microorganisms commonly present at soil. In the paper, there are stated results from testing of fine-grained concretes of different compositions, which were exposed to corrosive substances of biogenic origin. A great emphasis was especially put on observation of a silage effect on final physical-mechanical properties of concretes. Together with silage effects, effects of its components – acetic acid and lactic acid were also tested. These effects were compared with the corrosive effect of biogenic sulfuric acid. From current results, it was confirmed, that individual corrosive agents take part in a concrete degradation in a different extent. A concrete composition plays an important role in this process as well.

1. Introduction - theoretical

Concrete corrosion is characterized as a damage, deterioration and depreciation of concrete constructions by chemical and physical effects [1, 2, 3].

Rate of a concrete damage manifestation in a construction caused by chemical effects is dependent on a type of corrosive environment, which affects the given concrete. The effect on the concrete is caused by corrosive substances from the environment, transported to concrete components, which subsequently react with them. An important presumption for the chemical reaction is a presence of water, both in liquid and gaseous form. Building constructions could be eroded mainly by two types of a liquid environment, on the one hand by natural water and on the other hand by waste water [3, 4].

In most cases an acid corrosion is incurred by means of the present water environment. Because acids react mainly with calcium hydroxide and subsequently with calcium hydrosilicates and hydroaluminates to create calcium salts, a concrete corrosion rate is dependent on solubility of these salts and behaviour of a layer made of corrosion products. The more soluble the corrosion products are and the faster the wash out process is, the faster corrosion process is in the concrete mass as well. Binding components of a cement stone are changed by this process into a mass without binding properties.

Corrosion rate is determined on the one hand by a course of chemical reactions between the concrete and the corrosive environment and on the other hand by an exchange rate of the liquid medium close to the concrete surface. Gradual deterioration of the mass is therefore caused and it is accompanied with a creation of new reaction products. The layer of the reaction products is created gradually in dependence on a time of the corrosion action. The corrosion rate is considerable in the beginning but it decreases with growing of the reaction products. According to a range of experimental tests it can be stated, that the corrosion deterioration of the cement stone and the concrete is directly proportional to square root of the corrosion time [1, 3].

An important aspect for a progress and rate of the corrosion process is a concrete composition – a type of a binder system as well as a character of a used aggregate [3, 5, 6].

Many authors declare concrete results of their research on the corrosive environment effect on concrete constructions. Expression of the concrete deterioration degree is in these sources in the range of centimeters. For example, literature [7] states, that due to an effect of biogenic sulfuric acid in a sewage network the concrete deterioration is caused up to the depth of 30 mm after 5 years of exposure. It corresponds with research results [8], where a deterioration rate and a decrease of a surface layer is stated in a range of 3–6 mm/year.

2. Materials and methods

Aim of our experiment is to compare a deterioration degree of concrete specimens deposited for the exact time in corrosive solutions (media), which the most closely characterize corrosive agents arising within the agricultural activity or in the sewage network. The specimens made from the same concrete formula (and the same batch), deposited in water, were taken as a reference.

2.1. Testing methodology

The base of our testing was patterned from the standard method [9] for verification of a corrosion resistance of conventional compact concrete, made with cements based on Portland clinker, in the liquid corrosive environments. The verification of a resistance degree to corrosive solutions is conducted on concrete specimens. In the beginning the concrete specimens are deposited in defined solutions. After taking them from the solutions (interval 6 months) selected evaluating criteria are observed. These criteria are subsequently compared with the same parameters found out on specimens made of the same concrete, which were deposited for the same time in the standardized way.

2.2. Evaluating criteria

To basic evaluating parameters belong flexural strength, compressive strength, bulk density, water absorptivity and porosity. Evaluation of the deterioration degree of concrete surfaces was carried out also by means of polarizing and fluorescent microscopy. Testing of the deterioration degree of the concrete surfaces by means of a phenolphtalein indication solution was chosen as a supplementary method.

2.3. Verified mixtures of fine-grained concretes

For the planned experiment concrete specimens (20 × 20 × 100 mm) from fine-grained mixtures were made. Mixture composition was derived from the formula conventionally used for production of concrete prefabricated elements for agricultural structures (silage boxes, mangers, reservoirs, dungheaps) in the particular production plant. For the specimen production the same raw materials were used: aggregate of fraction 0/4 mm, Portland cement CEM I 42.5R, fly ash and blast furnace slag in ratio 60:20:20% (standard formula – marked as A); combination of CEM I 42.5R and fly ash in ratio 60:40% (formula P); only Portland cement CEM I 42.5R (formula C). Ratio aggregate:binder was in all the formulas ca. 3:1.

Note: For the reason of verification of previous results the same formulas were prepared with using CEM II/B-S 32.5R in the same ratios with blast furnace slag and fly ash – the formulas were marked as AII, PII, CII.

Test specimens were 1 day after production deposited in the environment with 90% humidity for 27 days. After that the specimens were prepared for the exposition in the selected testing media. The specimens from the individual formulas were deposited into the media separately, i.e. for each formula and the testing medium a separated testing vessel (a fish tank) was prepared.

2.4. Testing media
Within a solution of this research project we entered into a partnership with the Faculty of Natural Science, Department of Biochemistry in the Masaryk University in Brno. A selection of main initiators of corrosion actions in agricultural structures and a definition of tests solution representatives suitable for this experiment were carried out.

2.4.1. Testing in the test solutions prepared in the laboratory. This was the main direction of testing, for which the below described types of testing media were chosen:
Acetic acid. It is one of natural metabolites in living organisms. It can be usually found in plants, both as free acid and also as salts (acetates). It is contained in a significant amount in fermented fruits, as a subsequent fermentation product of a saccharide conversion.
Lactic acid. It is generated by a lactic fermentation of sugar, e.g. in milk, cheese and sauerkraut. This acid is together with the acetic acid a common component of the silage juices [10, 11].
Biogenic sulfuric acid. A representative of the corrosive medium, which is generated by actions of microorganisms occurring in soil and rocks [1]. A presence of the microorganisms (their type and amount) depends on a soil composition. In the case of biocorrosion by the biogenic sulfuric acid in the soil its progress and rate are dependent on a water amount, or rather on a soil humidity.
Silage extract. It is a leach from a silage prepared in a laboratory. Silage juices are composed of a cellular juice, which is released after mortification of plant cells, and of water, which is released by decomposition of organic substances. The juices released during an ensilage process are very corrosive, because they contain higher concentration of organic acids and other organic substances. pH of the silage juices is usually in values between 3.5–5 [10, 11].
Distilled water. It was used as a complementary corrosive medium.

Composition of the prepared testing solutions (stated in table 1) is based on findings and a research made by experts from the Masaryk University on real concentrations of individual corrosive agents present in the silage or in the excrements of farm animals.

Note: Methods and the used materials (and preliminary results of experiments as well) have been already reported in [12].

2.4.2. Testing in a freshly prepared silage. During the experiment another test was set up – this time the tested concrete specimens were deposited directly to a freshly prepared maize husks. Under exactly fixed conditions the silage was created in the course of 6 weeks. The silage preparation, an analysis of its quality as well as its subsequent observation during the test were carried out in a specialized laboratory.

3. Results and discussion
Research works during the experiment were divided into several directions.

3.1. Observation of a testing media condition

3.1.1. Testing solutions. From the beginning of the experiments a measurement of media pH and a visual evaluation of their condition (turbidity, change of colour) in the same time were conducted. Shortly after the deposition of the concrete specimens into the test media a change of pH was noticed due to substantial concrete alkalinity (pH = ca. 13). Selected values of solution pH (from the time of deposition of the specimens) in the course of time are stated in Table 1. The use of biogenic sulfuric acid was based on a fact that sulfate (bio)corrosion, caused by this acid, is well known. The comparison of corrosion effects between organic (bio)products and a typical inorganic (bio)product brings a new approach of the study.

Table 1. pH of media with the deposited specimens made from the standard formula A.

Medium		pH				
		before deposition	14 days of deposition	90 days of deposition	180 days of deposition	360 days of deposition
MED **1**	distilled water	5.50	12.05	11.95	11.46	12.10
MED **2**	lactic acid	1.31	4.75	5.66	7.40	7.14
MED **3**	acetic acid	3.40	10.99	11.62	11.75	10.89
MED **4**	biogenic sulfuric acid	1.20	1.38	6.86	6.82	6.09
MED **5**	silage extract	3.29	6.88	8.87	9.73	9.14

From the Table 1 it follows, that shortly after the beginning of the experiment a rapid growth of pH values occurred in the individual testing media. It is therefore obvious, that in the later time the acetic acid, the lactic acid and the biogenic sulfuric acid had no impact on the concrete specimens, but there was an effect of their salts.

3.1.2. Silage. In the specialized laboratory analyses of the ready-made silage were carried out (i.e. 6 weeks after its setting) and after that a silage quality was evaluated in the interval of 6 months (every time within taking of the concrete samples from the silage). Results (mean values from 3 parallel tests) are stated in Table 2.

Table 2. Analyses of the silage in the course of time.

Parameter	Unit	Silage		
		6 weeks	6 months	1 year
Dry matter of the original mass	%	32.27	33.42	31.31
pH	-	3.80	3.94	4.10
Ammonia	g/kg of the dry matter	0.52	0.71	1.10
Ethanol	% of the dry matter	0.32	0.013	0.077
Acetic acid	% of the dry matter	3.94	0.87	1.87
Lactic acid	% of the dry matter	8.13	6.89	7.81

According to analyses results, the fresh maize silage was evaluated as a product of very high quality. From the analyses results of the silage in the age of 1 year with parameters of the fermentation process of the maize silage published in the literature [10] followed, that the silage keeps the same quality and all the time fulfils all the requirements (put on the silage from the point of view of farm animals´ nutrition).

Determined maximum content of the acetic acid reached a value of 2.1%, which corresponds with published values in [10]. For the common maize silage maximum values of the lactic acid content in a degree of 7% are stated, under right fermentation conditions even values over 8% are published [11].

Note: Ammonia content is not usually stated for the maize silages, the determined ammonia contents are low and show a growth according to the date of sampling as a consequence of a proceeding of proteolysis of nitrogen substances.

3.2. Visual assessment

Within each sampling of the concrete specimens from the test media their large photo documentation was carried out and their condition was visually evaluated.

3.2.1. Samples from the testing solutions. Each testing medium demonstrated a different effect on the tested concrete specimens. The specimens deposited for a period of 1 year in distilled water (MED 1) and the acetic acid (MED 3) showed no surface deterioration. A surface of the concrete specimens removed from the biogenic sulfuric acid (MED 4) showed signs of a severe deterioration – a well-marked porous structure of a cement binder, a deteriorated layer had a pasty character. In the lactic acid (MED 2) a change of colour occurred on the concrete specimens. Samples from the formulas C and P significantly changed to a rusty colour, the others had black coloured surfaces. Products of crystallization were noticeable on the specimens from the formulas C and P. It was about white fine little stars or flakes. Crystals appeared also on the specimens from the formula CII. In this case they have a regular crystallization structure and black-grey colour. On the tested specimens exposed in the silage extract (MED 5) a significant growth of hard reaction products of brown colour was noticeable (it was impossible to scrape them off). The most significant difference between the specimen state after their first and second sampling from the test media is in the extend of reaction products´ growth in the compositions C and CII. More detailed description of the concrete degradation observed in this experiment is given in [12].

3.2.2. Samples from the silage. The specimens deposited in the silage were after the end of exposition cleaned at first and after that a visual evaluation of their degradation degree were done. On the specimens there was a significant demonstration of a direct contact with the silage and its influence. A colouring in a different extend occurred on the surface (uneven spots), which is caused by effect of an uneven covering by the maize husks in the beginning of the experiment.

3.3. Testing of physical-mechanical properties

The specimens made from fine-grained concretes taken from the test media were subjected to a set of tests in terms of physical-mechanical or physical-chemical properties.

3.3.1. Samples from the testing solutions. From the technological point of view the most important parameter for the assessment of the concrete resistance to the corrosion environment is a development of strength and other characteristic properties of concrete. Test results of the strength characteristics of the concrete specimens found out after 12 months of the deposition in the test solutions are depicted in Figure 1.

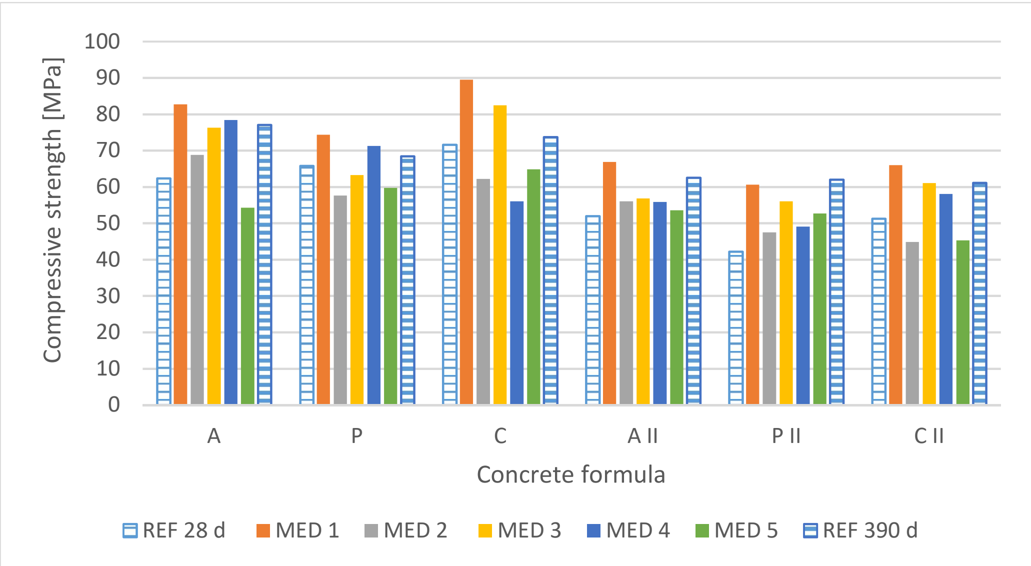

Figure 1. Effect of the testing media on values of compressive strength of the individual concrete formulas in comparison with strength of the reference specimens deposited in the standard conditions (formulas A, P, C prepared with CEM I 42.5R; formulas AII, PII, CII prepared with CEM II/B-S 32.5R) – deposition time 1 year.

3.3.2. Samples from the silage. The specimens taken from the silage were also evaluated preferentially from the point of view of the strength characteristics. Their development in the course of deposition in the silage is depicted in Figure 2 and 3.

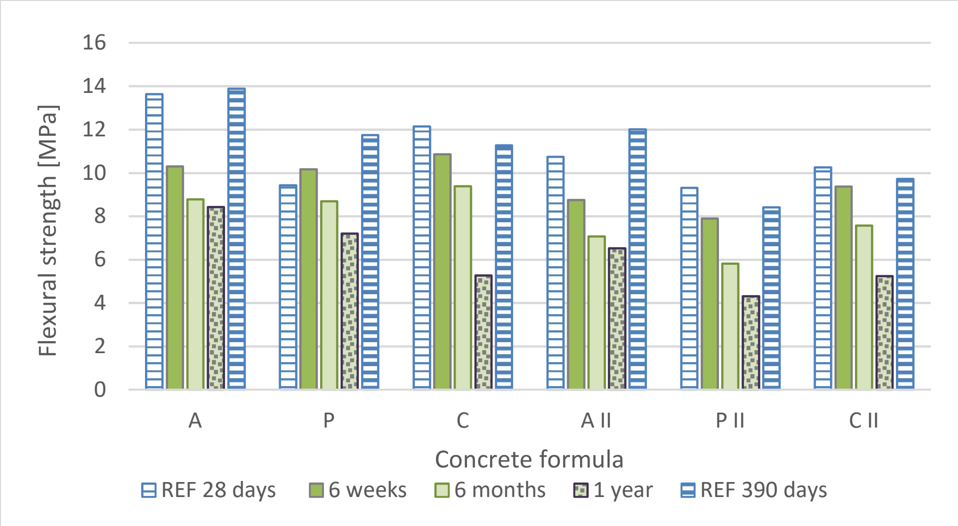

Figure 2. Effect of the long-term deposition in the silage on values of flexural strength of the individual concrete formulas in comparison with strength of the reference specimens deposited in the standard conditions (formulas A, P, C prepared with CEM I 42.5R; formulas AII, PII, CII prepared with CEM II/B-S 32.5R).

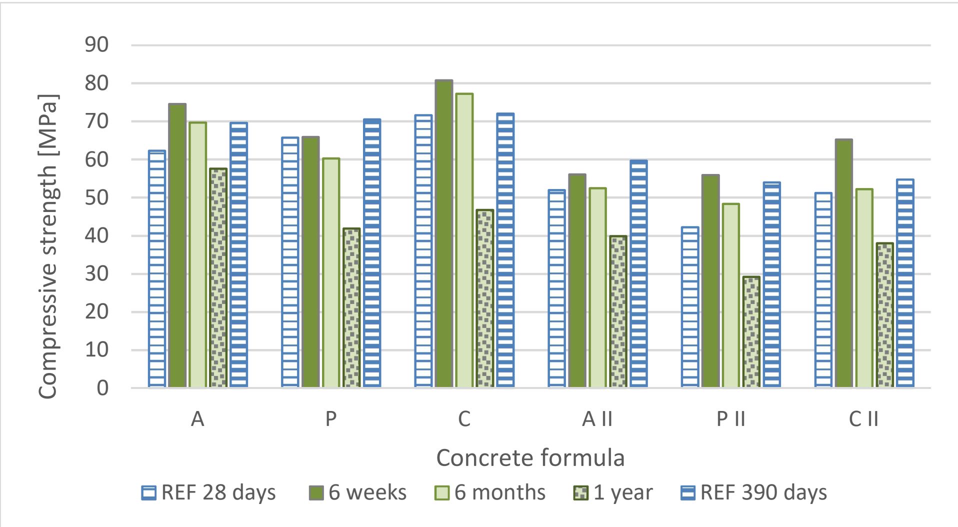

Figure 3. Effect of the long-term deposition in the silage on values of compressive strength of the individual concrete formulas in comparison with strength of the reference specimens deposited in the standard conditions (formulas A, P, C prepared with CEM I 42.5R; formulas AII, PII, CII prepared with CEM II/B-S 32.5R).

From the results depicted in Figures 2 and 3 it is obvious, that after 6 weeks from deposition into the maize husks due to its humidity the growth of the compressive strength within the concrete specimens of all formulas occurred (see the left hatched column and the column next to it). Due to the long-term deposition of the concrete in the silage a degradation of the surface layers of the concrete

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specimens occurred together with a significant infiltration of the silage juices to the concrete mass via its porous structure.

The specimens deposited for 1 year in the silage after the flexural strength test were subjected to another test with phenolphtalein, which enables to evaluate a rate and a depth of the degradation of the surface layer of the concrete specimens. The result is possible to observe in Figure 4. The photographs complete or confirm the results depicted in the graphs in Figure 2 and 3.

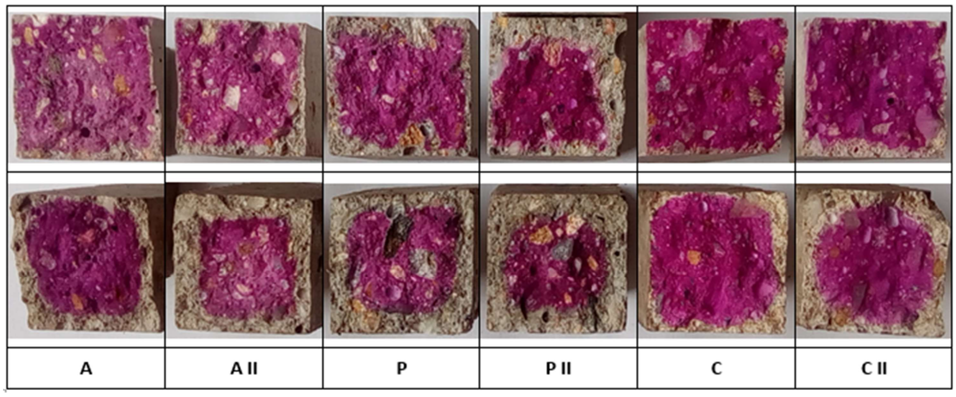

Figure 4. Comparison of the degradation of the surface layers of the specimens of the evaluated concrete formulas (reaction on a fraction area – the test with phenolphtalein) – the reference specimens deposited during their curing in the place with 90% humidity are above, the specimens deposited in the silage for 1 year are below.

4. Conclusions

Effect of the testing media prepared in the laboratory on the specimens deposited for 6 and 12 months is really significant. The surface deterioration is mostly visible on the specimens deposited in the lactic acid (MED 2), the biogenic sulfuric acid (MED 4) and in the silage extract (MED 5). On the specimens (especially from the formula C) deposited in the silage extract it was possible to observe the uneven growth of the solid reaction products of brown colour, which affected the degree of the strength characteristics comparing to the other formulas. The biggest influence on the degradation of the specimens was evaluated for the biogenic sulfuric acid, the inorganic (bio)product, which was used as a comparative agent with the organic (bio)products.

Comparing the lactic acid (MED 2) and the silage extract (MED 5), it can be concluded, that the effect of these testing media on the strength characteristics of the concrete specimens is very similar. An exception was the formula A, for which the medium 5 had the significantly negative effect.

From the testing of the concrete specimens deposited in the silage can be concluded, that the effect of the silage juices is substantial. The best resistance was demonstrated by the formula A. In the case of the formulas CII and AII prepared with CEM II their strength characteristics were comparable with the results for the formula P. We can therefore declare, that the formulas AII and CII are more resistant to the silage effect comparing with the formula P, which under standard conditions of curing demonstrated higher strength characteristics compared to the formulas AII and CII. The worst results after 1 year-long silage effect were detected for the formula PII.

Comparing the results of the strength characteristics of the concretes deposited in the silage extract prepared in the laboratory (or rather the lactic acid, which is a component of real silage juices) and the specimens deposited directly in the silage it is obvious, that the silage extract has not the same effect on the concrete as the silage. Only in the case of the formula A the effect of both media types was comparable. In the other cases the direct silage effect (1 year-exposition) on the concrete specimens had significantly more negative impact than the effect of the silage extract.

The real silage demonstrated higher effect on the degradation of the all concrete formulas comparing with the corrosive effect of the biogenic sulfuric acid, which in our experiment represented a completely

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different mechanism of corrosion and therefore served for the comparison of the different corrosive effects.

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