

Experimental verification of concrete resistance against effect of low pH

D Dobias¹, S Rehacek¹, P Pokorny¹, D Citek¹ and J Kolisko²

¹ Research Engineers, Klokner Institute CTU in Prague, Prague, Czech Republic

² Head of department, Klokner Institute CTU in Prague, Prague, Czech Republic

E-mail: daniel.dobias@cvut.cz

Abstract. In the introductory part of this article, the principles of a concrete degradation by organic acids are mentioned, these acids occur, particularly in silage and haylage troughs, biogas stations, on concrete floors and grates in the vicinity of drinking basins with an addition of formic acid and also in fermenters and slurry reservoirs. In the experimental part, the first results of monitoring resistance of a concrete with a sealing admixture on the basis of styrene-acrylate against an effect of a low pH are presented. Additional accompanying tests are stated in the tested concretes.

1. Introduction

A method of preserving by so called ensiling is used for preservation of feed for farm animals in the Czech Republic, which is a fermentation process, in which the feed (maize, fodder plants, sunflowers, etc., a maximum dry weight is 45-50 %) is stored in silage pits under constant compaction (e.g. by packing down or rolling with tractors), in which the feed is closed hermetically. In this method of preservation, in contrast to making hay, is the feed (silage) stored in a sappy state. The most frequent material for the construction of the walls and the bottom of the silage pit is the concrete. In some cases, the asphalt concrete is used for making the bottom, which is more resistant than the concrete from the point of view of the resistance to the effect of acidic silage juices. Preservation of the feed takes place by the action of lactic fermentation of sugars contained in the ensiled feed without access of air, while the content of nutrients as well as vitamins is maintained. In order to maintain the highest quality of the silage, it is necessary to create a sufficient amount of lactic acid as soon as possible, which is a basic preservative agent. The pH of the silage is usually lower than 4. Due to the acidic environment, by limiting the access of air along with the production of CO₂, which is produced by food, respiration and microbial activity, an anaerobic environment is created, in which no putrid processes occur. If the technological discipline of the silage preparation is not observed or if the unsuitable fodder is used, there is an aerobic degradation - putrefaction. During this process, a butyric acid, acetic acid or formic acid comes into existence, which debases the silage (in addition it takes part in the degradation of the concrete) [1, 2].

With regard to the acidic environment, especially of the silage and haylage pits, biogas stations and concrete floors and grates in the vicinity of the drinking basins with water acidified with lactic acid, it is used the concrete in the degree of the environmental influence XC4, XF4, XA3. For these degrees of the environmental influence is determined the minimum strength class C 30/37. ČSN EN 206 and ČSN P 74 2304 determines for the concrete C 30/37 XC4, XF4, XA3 these minimum requirements [3 and 4]:

- Maximum water coefficient $w = 0.45$



- Minimum cement content = 360 kg/m³
- Minimum air content = 4%
- Maximum depth of penetration with pressure water = 20 mm

In view of the fact that a larger amount of sulphates usually does not occur in the silage juices, it is not necessary to use sulphate-resisting cement according to ČSN EN 206 and ČSN P 74 2304.

2. Description of concrete degradation

The silage juices are organic acids constituted especially by lactic acid (in case of improper course of ensiling, the butyric acid, acetic acid or formic acid is formed). The volume and acidity of the juices fluctuate during fermentation and depends on the type of the stored feed and its moisture content at the start of ensiling. The volume of the silage juices further depends on the tightness of a cover plastic film, which should prevent from in-leak of rainwater into the silage. In-leak of rainwater occurs especially along the walls. It is substantiated, that the pH of the silage juices ranges from 2.5-4. Due to the influence of the effect of these very acidic juices, the degradation of the surface layer of the concrete occurs already in a very short time (and even after one year of use). The primary damage of the concrete is usually local, in areas, where there is the concentration of the acidic juices, usually to the depths of 1-5 mm. Cement lute on the surface of the concrete of the walls and the slab is disrupted to incohesive grains and there is the exposure of the coarse grains of the aggregate.

The low resistance of the concrete to the effect of the acidic environment of the silage juices is due to its high alkalinity (but the pH of the young concrete is higher than 13). The reaction of the acidic juices with cement hydration products causes corrosion of the type II. The corrosion of the type II is characterized such that the solutions, which penetrate into capillary-pored structure of the concrete, react with a cement matrix and the result of these reactions is the formation of the easily soluble compounds. The cement matrix is decomposed gradually, loses its binding properties and as a result of this, the mechanical properties of the concrete are reduced. In the initial phase, the portlandite Ca(OH)_2 is "attacked" at first and subsequently the other components of the cement lute so called hydrosilicates and calcium hydroaluminates are decomposed to form calcium salts. The rate of the concrete depends on solubility of these calcium salts and on the behaviour of the layer of the corrosion product, which has arisen. The more are the reaction products soluble and the faster they are washed out of the concrete, the faster the degradation occurs. The rate of the corrosion processes is dependent on it, whether the reaction products cling to the surface of the concrete or whether they are washed away. In the case of clinging to the surface of the concrete, the reaction products help to slow down the access of the acidic juices. During withdrawal of silage, due to mechanical action of the withdrawal device of the loader, the abrasion against the concrete of the wall and the floor slab occurs and thus the acceleration of the acid's action on the newly opened surface of the cement lute [5 and 6].

It is evident from the literature [7, 8], that the development of the concrete admixtures warranting the increase in the resistance to the effect of acidic environment ($\text{pH} < 7$) is currently limited to modified polymer dispersions with low additions of substances with the ability to modify more often the physical properties of mixtures than the actual concrete after setting. Products, which are intended for application directly to the concrete, are very limited amount on the market (Czech Republic + EU). It can be said about all of these products that they are a certain form of analogy to the products intended for the surface protection of concrete products with the aim of creating a reliable and long-term effective insulation between the surface of the concrete and the acidic environment.

As the application admixtures warranting the increase in the concrete resistance to the acidic environment, these are always based on the polymer dispersion more often of copolymer frame. Primarily, the polymers and copolymers on an acrylate basis were tested (acrylates, styrene-acrylates, styrene-acrylate esters). Also the before available copolymers of butadiene-styrene were tested (currently elastomeric base), alternatively the copolymers of vinyl alcohol. At the present, in this case, mainly the copolymers of styrene-acrylate are used, since they primarily evince the highest resistance to the effect of the alkaline environment (problems of the strongly alkaline pH of the porous concrete solution) from all mentioned. Their use is now mainly as redispersible dispersion powders when specifying the recipe for the preparation of plasters for thermal insulation systems. The main task of dispersions is hardening of a conventional silicate binder (dispersion has binding properties) and the

reduction of an usual porosity of the concrete and thus decrease in an absorption capacity and permeability of the concrete for aqueous solutions. The organic connective dispersion base ensures better cohesiveness between the aggregate and the silicate binder during its sloughing due to the acidic solutions.

In our experimental works, we focused on the use of the sealing admixture on the basis of styrene-acrylate in various doses directly into the concrete mixture. The goal is to create the concrete with high tightness, density and resistance to the aggressive media over the whole cross section of the created constructional element.

3. Experimental part

In the experimental program, the test of the long-term monitoring of the effect of formic acid on five concretes with different composition was started, see table 1. The reason for using formic acid is frequent addition directly as the additive to silages and is also used to adjust the pH of water in the drinking basins. The pH of water in the drinking basins is then around 4. In order to achieve the highest density, the low water coefficient was used using the plasticizing admixture and the consistency of SI (subsidence 0 mm) was used intentionally. This consistency is used on some prefabricated components for the production of vibrocompressed goods intended for use in agriculture (troughs, grates, slabs, pillars, etc.). In some recipes, the sealing admixture was used with the goal to determine the influence of this sealing admixture on the resistance to the effect of the acidic environment. The dose of the sealing admixture was chosen with regard to the economic acceptability of the recipes. The parameters of both fresh concrete (temperature, volume weight, subsidence of cone), and the time course of the compressive strength (at the age of 1, 7, 28, 60 and 90 days) and the depth of penetration through pressure water (at the age of 28 days) were monitored (table 2). For each test term, three test specimens were made for each recipe.

Table 1. Composition of concretes.

Components	Recipe designation, doses in kg / m ³				
	I	II	III	IV	V
CEM I 42,5 R	390	200	200	200	390
Slag	0	190	190	190	0
Water	135	123	114	114	114
Sand 0/4	1110	1110	1110	1110	1110
Ballast 4/8	600	600	600	600	600
Plasticizer	2.7	2.7	2.7	2.7	2.7
Sealing admixture	0	0	2	7	7
Water coefficient, k-value for slag = 0.6	0.346	0.391	0.369	0.358	0.310
Water coefficient, k-value for slag = 1	0.346	0.315	0.297	0.310	0.310

The concrete compressive strength was determined at cubes with an edge of 150 mm according to the norm ČSN EN 12 390-3 [9, 10]. The depth of penetration through the pressure water was also performed on the cubes with the edge of 150 mm according to the norm ČSN EN 12 390-8 [11]. For the long-term monitoring of the concrete in the acidic environment, three cubes with the edge of 150 mm were made from each recipe. These cubes were placed in the 500 L tank with formic acid, whose pH is maintained at the value of 3 continuously (in practice, the pH ranges from 2.8-3.2), after 28 days of aging. The pH value is checked at weekly interval using a pH meter. The depth of degradation is observed on the cubes, the weight loss is monitored and the photo-documentation of the appearance change is performed.

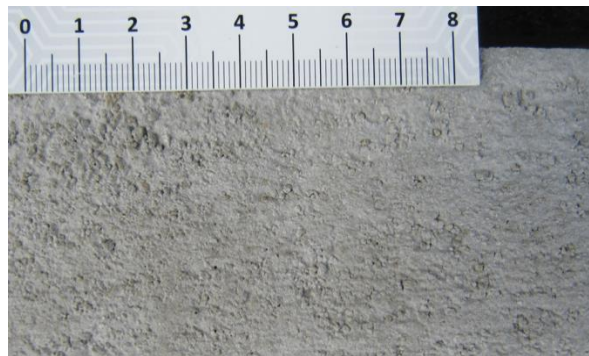
Table 2. Properties of proposed concretes.

Properties	Recipe designation				
	I	II	III	IV	V
Subsidence of cone [mm]	0	0	0	0	0
Temperature of fresh concrete [°C]	22.5	21.2	21.0	21.3	23.0
Volume weight [kg/m ³]	2260	2250	2280	2260	2260
Depth of penetration [mm]	12	12	9	6	6
Compressive strength [MPa] at the age of:					
1 day	15.6	8.3	7.5	7.9	16.3
7 days	43.0	27.6	30.7	26.5	44.1
28 days	48.0	52.2	48.1	45.6	47.9
60 days	51.0	54.0	57.3	51.5	50.6
90 days	53.5	54.9	57.5	55.5	52.5

Note: For this type of the mixture is more suitable to use the VeBe test for the determination of the consistency of the fresh concrete.

A visual description of the concrete degradation of the test specimens (the cube with the edge of 150 mm) after 90 days of exposure:

- I and V – significant colour changes on the surface – “yellowing”, surface degradation to the depth of about 1,5 mm (‘figure 2’)
- II to IV – small colour changes on the surface, surface degradation to the depth of about 0.5 mm (‘figure 3’)
- I x V – an influence of the sealing admixture was not observed
- II x III x IV – an influence of the sealing admixture was not observed

**Figure 1.** The surface of the reference specimen**Figure 2.** Surface of the test specimens I and V**Figure 3.** Surface of the test specimens II, III, IV

4. Conclusion

Based on the results of the concrete compressive strength, it is possible to state that the concrete can be classified into the strength class C 30/37 and should satisfy for the classification into the degree of the environmental influence XA3. It should be noted that the results are, to a certain extent, influenced by the used dose of mixing water, which was processed so that the mixtures have the same workability. The slag has the positive influence on the reduction of mixing water dose, the influence of the sealing admixture on the decrease of mixing water is not significant (2-4 L/m³). The rate of increase of compressive strength in the recipes with slag (II – IV) is slower (especially in the age of 1-7 days), and all recipes reach the similar strengths at the age of 28 days. Thanks to latent hydraulicity is the strength in the slag recipes at the age of 90 days higher approx. by 5 % in comparison with the recipes without slag. The influence of slag on the depth of penetration through the pressure water was not observed.

The sealing admixture has the influence in particular on reduction of the depth of penetration of pressure water up to 50 %. Already after two months, when the samples were exposed to the acidic environment (formic acid, pH = 3), the differences in the progress of degradation of the concrete surface are evident. In the concretes without slag, there was the significant colour change “yellowing” and washing out the concrete surface up to the depth of about 1 mm. The influence of the sealing admixture on reducing the degradation progress has not been demonstrated yet.

It can be stated that already after a relatively short exposure of the concretes in the simulated environment of the silage pits is evident that despite the design of the concrete in the highest degree of the environmental influence (XC4, XF4, XA3) there is the relatively rapid degradation (decomposition of cement lute) of the surface layer of the concrete due to the influence of the acidic silage juices. It is necessary to mention that the highest degree of the chemical influence of the environment XA3 is designated for the environment with the pH ≥ 4 , where the environment of the silage juices is significantly more aggressive, the pH is usually 3-4. The concrete degradation test in the experimental tank will continue, with the goal to determine the rate and progress of degradation of the concrete and the comparison of the influence of the slag and the used sealing admixture and its dose.

5. References

- [1] Gebrehanna M M, Gordon R J, Madani A, VanderZaag A C and Wood J D 2014 Silage Effluent Management: A Review *Journal of Environmental Management* **143** 113-122.
- [2] Beddoe R E and Schmidt K 2009 Acid Attack on Concrete - Effect of Concrete Composition; Part 1 *Cement International* **7** 88-94.
- [3] EN 206:2014 Concrete – Specification, performance, production and conformity
- [4] ČSN P 74 0423 Concrete – Specification, performance, production and conformity – Additional information
- [5] Al-Tamimi A K and Sonebi M 2003 Assessment of Self-Compacting Concrete Immersed in Acidic Solutions *Journal of Materials in Civil Engineering* **15** 354-357.
- [6] Sernad A, Yazici H, Yigiter H and Baradan B 2007 Sulfuric Acid Resistance of High-volume Fly Ash Concrete *Building and Environment* **42** 717-721.
- [7] Monteny J, De Belie N, and Taerwe L 2003 Resistance of Different Types of Concrete Mixtures to Sulfuric Acid *Materials and Structures* **36** 242-249.
- [8] Sokolowska J J, Woyciechowski P and Adamczewski G 2013, Influence of Acidic Environments on Cement and Polymer-cement Concretes Degradation *Advanced Materials Research*, **687** 144-149.
- [9] EN 12390-3:2009 Testing hardened concrete - Part 3: Compressive strength of test specimens.
- [10] EN 12390-7:2009 Testing hardened concrete - Part 7: Density of hardened concrete.
- [11] EN 12390-8:2009 Testing hardened concrete - Part 8: Depth of penetration of water under press.

Acknowledgment

The paper was drawn up with the assistance of TACR (Technology Agency of the Czech Republic) grant TH02020690 “The concrete with excellent resistance under aggressive media condition”.