Improved chemical resistance of concrete by incorporation of industrial waste

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Abstract

The paper covers a part of development of concrete prefabricates with improved durability for silage pits and other special applications. The role of concrete composition containing fly ash and combination of fly ash and ground granulated blast furnace slag on its chemical resistance was studied. The test of resistance to selected aggressive solutions was carried out by placing concrete samples in defined aggressive solutions and, after removal from the solutions, deteriorated samples were compared with test samples of the same concrete mixes cured according to standard EN 196. The development of flexural and compressive strength of reference and deteriorated samples in aggressive solutions was monitored. Microstructure and the mechanism of chemical degradation of concrete surface was evaluated by light microscopy using transmitted, reflected and fluorescent light. Phase composition of reaction products was determined by X-ray powder diffraction. Brown calcite efflorescence forms crust on samples stored in silage effluent. Corroded, uncorroded and buffer layer in concrete were described supported by direct observation in microscope. Samples with admixtures are more resistant to sulfuric acid showing better strengths compared to reference concrete.

Keywords

Concrete, chemical resistance, admixtures, microscopy, strength, reaction products

Introduction

Microorganisms accelerate the deterioration of concrete elements by produced sulfuric acid in a process of microbially induced concrete corrosion (MICC) [1]. MICC and the corrosion process in sewer pipes and pipeline junctions have been extensively studied [2, 3]. These studies claimed that the highest deterioration occurred when high concentrations of hydrogen sulfide, moisture and oxygen were present. These conditions are favourable for microbial (Thiobacillus) activity. The rate and extent of MICC on three different concrete mix during initial chemical pH reduction was studied [4]. Three stages of MICC was formulated by Islander at al. [5]. The process can be described by the 3 following steps: concrete surface neutralization providing appropriate environment for sulfur oxidizing bacteria (SOB) to grow, sulfuric acid (H_2SO_4) production by SOB on concrete surface and chemical reaction between H_2SO_4 and cement hydration products [6].

Silage effluent must be effectively managed and collected because it poses a considerable pollution threat [7]. The reactions between the acidic silage effluent and cement hydrates produce calcium salts which are highly soluble [8]. This degradation process has been observed to erode concrete progressively and may be accelerated by various mechanical actions such as high-pressure cleaning [9].

The concrete degradation is characterized by a corroded layer of high porosity. The thickness of the layer is determined by the combination of dissolution, precipitation and transport process which depend on cement chemical composition, binder reactivity, aggregate reactivity, grading curve as well as concrete composition [10, 11]. Experiments have shown that the corrosion resistance of concrete depends on the type and chemical composition of the cement as well as the pH of the attacking acid [11]. The dissolution of ferrite or aluminate hydrates and the corresponding loss of Fe³⁺ and Al³⁺ is slower and occurs at lower pH values than the release of Ca²⁺ from C–S–H and calcium hydroxide [12, 13]. The corroded layer comprises zones of varying composition and structure determined by the different pH-stabilities of the hydration products and the solubility of the dissolved ions with respect to pH [14].

The role of improvements in acid resistance with silica fume and fly ash have been achieved by concrete designed to maximize particle packing [15]. The effect of silica fume and fly ash on corrosion resistance is essentially due to their residual volume in the corroded layer and the contribution of their hydration products to neutralization capacity [16]. In case of Portland blast furnace cement, the neutralization capacity of the binder is given by its total CaO content [10].

The objective of laboratory testing was to compare the rate of degradation of concrete test bodies stored over defined period of time in aggressive solutions. The role of admixtures on concrete resistance was studied by means of polarizing and fluorescent microscopy and strength development. The phase composition of reaction products was determined by X-ray powder diffraction.

Materials and Methods

Series of concrete samples with industrial wastes incorporated in mix design were tested in aggressive environment of various acids. Aggressive solutions were developed and designed in cooperation with Department of Biochemistry at Masaryk University Brno. In the beginning of the project, the main agents of the corrosion of concrete that occur in agricultural buildings were selected. (Table 1).

The concrete binder was based on cements CEM I 42.5 R (Hranice, CZE) and CEM II 32.5 R (Ladce, SK) which were blended with fly ash (FA) (Rybník, PL) and blast-furnace slag (BFS) VJM (CEMEX – Dětmarovice, CZE). The fine aggregate 0-4 mm from Mohelnice (CZE) was used. Reference samples of concrete were correlated with concretes with partial replacement of cement by fly ash and combination of fly ash and ground granulated blast furnace slag. Concrete mix design is given in Table 2.

Reference samples were stored in distilled water. Simultaneously, samples of concrete from test aggressive media and reference samples were tested. Flexural and compressive strength according to EN 196 was monitored after 12 and 20 months.

The assessment of the degree of surface deterioration of concrete samples was done by polarization and fluorescence microscopy on thin sections. Section was oriented across the specimen to be able to measure the depth of corroded layer. All thin sections of concrete were impregnated with epoxy mixed with fluorescent dye (Struers, EpoDye) to accentuate the pores and cracks in concrete. Microscopic observation was done on Nikon ECLIPSE LV100ND with epi illuminator LV-UEPI2 (excitation filter 330-380, dichroic mirror 400, barrier filter 420). Besides fluorescent regime FL and reflected light RL, the samples were examined in bright field microscopy under dia illumination in PPL (plane polarizers) and XPL (crossed polarizers). Pictures were taken with attached digital camera. Relatively long exposition times (20-30 sec) and low intensity of UV-A light (depending on magnification) were used to achieve good contrast of pictures in fluorescent regime.

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Table Aggreg	SIVE Environm	ients for accelers	ated degradation	of concrete
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		pH						
		before	14	90	180	360	570	
		storage						
		days						
distilled water	ref	5.5	12.05	11.95	11.46	11.88	11.13	
lactic acid	LA	1.31	4.75	5.66	7.4	7.14	7.77	
acetic acid	AA	3.4	10.99	11.62	12.75	10.89	10.54	
sulfuric acid (biogenic)	SA	1.2	1.38	6.86	6.82	6.07	7.05	
silage effluent	SE	3.29	6.88	8.87	9.73	9.14	9.2	

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	А	Р	С	AII	PII	CII
Aggregate [Mohelnice] 0-4 mm	5.420	5.420	5.420	5.420	5.420	5.420
CEM I 42.5 R [Hranice, CZE]	1.040	1.040	1.704	-	-	-
CEM II 32.5 R [Ladce, SK]	-	-	-	1.040	1.040	1.704
Fly ash [Rybník, PL]	0.400	0.700	-	0.400	0.700	-
Slag VJM [CEMEX – Dětmarovice, CZE]	0.400	-	-	0.400	-	-
Superplasticizer - Stachement 2180	0.012	0.012	0.012	0.012	0.012	0.012
water	0.880	0.850	0.880	0.880	0.850	0.880

Reaction products formed on surface of the sample C, the sample with the most distinct efflorescence, was determined by X-ray powder diffraction. The qualitative analysis was done by Bruker D8 Advance with Cu anode ($\lambda K\alpha$ =1,54184 Å) and variable divergence slits at Θ - Θ Bragg-Brentano reflective geometry. Powder samples were placed in zero background sample holder.

Results and discussion

Phase composition

Phase composition of reaction products in form of various efflorescence on surface of C samples was determined by powder X-ray diffraction. Calcite was detected in all C samples. Reaction products of samples stored in lactic acid were bassanite – $CaSO_4 \cdot 0.5H_2O$, gibbsite – $Al(OH)_3$, quartz – SiO_2 , chrysoberyl – $BeAl_2O_4$ and various salts and esters of lactic acid. Gypsum, ettringite, arcanite and quartz formed reaction products in samples attacked by biogenic sulfur acid. Quartz and szomolnokite $FeSO_4 \cdot H_2O$ were evaluated in samples stored in silage effluent. Brown colour of efflorescent can be related to oxidation of ferrous oxide in calcite. Individual XRD testing of efflorescence on samples stored in silage effluent showed only calcite and quartz contents. Some of the reaction products were precipitated on surface of solution. In case of lactic and acetic acid, these surface precipitates consist of calcite, quartz and sylvite – KCl. Based on these results of phase analysis direct observation of reaction products was done in PPL and XPL in microscope.

Samples show visible deterioration of surface especially in case of samples stored in lactic acid, biogenic sulfuric acid and silage extract. The concrete samples stored in lactic acid were stained black due to exposure to bacteria, biogenic sulfuric acid caused the most visible disruption of the sample surface; after removal from the medium, the surface was smear and a small recess formed. Numerical models were proposed for the loss of surface material due to abrasive processes and gypsum precipitation during sulfuric acid attack by previous study [13]. Expansive process related to formation of ettringite or gypsum in attacked concrete closely related to pH was described in [17, 18]. It was reported that below pH 10.7 ettringite starts to decompose into gypsum. Samples stored in silage extract showed an uneven solid brown calcite efflorescence (**Fig. 1**).



Fig. 1 Calcite efflorescence on samples stored in silage effluent

Microscopy

Samples of concretes exposed to acidic solutions for 6 months were studied in epi (PPL, XPL) and dia (FL, RL) illumination on polarization microscopy comparing the role of aggressive media with reference sample stored in distilled water in terms of optical properties. The corroded layer formed due to action of acidic solutions was characterized in detail. Microscopical evaluation (**Fig. 1**) was carried on petrographic thin section with fluorescent dye to accentuate microcracks and pores in concrete. Not only large pores, but also layer of different porosity can be distinguished in FL. Brighter colours represent zones of higher porosity with increased content of epoxy with fluorescent dye. Examination of exposed samples in FL allows to monitor the depth of corroded layer in concrete. This layer has higher porosity compared to uncorroded concrete with distinctly brightly colours (**Fig. 2**). All but cubic crystalline as the products of neutralization reaction of alkaline binder with acidic solution show birefringence in XPL in dia illumination. Since the birefringence is dependent on orientation to optical axes, the orientation of newly formed hydrates can be studied as well. In case of silage effluent, the concentric rims structure can be observed with various thickness on the surface of samples (**Fig. 3**).

Observation in transmitted light confirms the presence of aggregates of white to yellowish white massive to tabular crystals of gypsum on the surface of samples stored in biogenic sulfur acid. Between zone of gypsum crystals aggregates and uncorroded concrete, there is zone of increased porosity in the place of former binder and unreacted quartz aggregate (**Fig. 4**).

Samples stored in silage effluent show szolmnokite, described in nature as secondary mineral of pyrite-rich oxidized sulfide deposits formed under highly acid conditions, presented in form of radial aggregates of fibrous white to brown crystals in voids. Massive efflorescence on the concrete surface is calcite as the products of carbonation of salts of lactate acid. The presence of carbonate in efflorescence, fizzing in contact, was proved by drop of 35% HCl. Layered microstructure showing continuous browning of layers can be related to oxidation of Fe²⁺ or reduction formation of ferroan calcite (calcite with trace amounts of Fe²⁺), often described in diagenetic process (**Fig. 3**). The effect of Fe²⁺ and Fe³⁺ on nucleation of CaCO₃ was previously studied [19], seeing the higher solution pH (> 6.5), iron hydroxide forming before the onset of CaCO₃ precipitation and playing a role of seed permitting to initiate CaCO₃ nucleation. There are various sources of iron in concrete that can be optimized to support the formation of calcite efflorescence which might serve as a protective layer on concrete. Nevertheless, this mechanism is only applicable in narrow range of pH 7-8 in reducing conditions.

The alkaline binder of all samples is dissolved vividly in reaction with acidic pore solution forming soluble salts. The depth of corroded layer depends on many factors. The processes affecting the reaction kinetics [10, 20] of binder dissolution is related to consumption of proton H^+ and dissolution of Ca^{2+} , Fe^{3+} and Al^{3+} and neutralization capacity of the binder constituents C-S-H and portlandite (CH).



Fig. 2 Zones of corroded (green color – fluorescent dye) and uncorroded concrete, sample PII in silage effluent after 6 months, FL



Fig. 3 Radial fibrous calcite and szolmnokite in voids and layered spheritic fibrous calcite on the surface, sample C stored in silage effluent after 6 months, PPL



Fig. 4 Layer of crystalline gypsum on the surface of CII stored in biogenic sulfuric acid after 6 months, PPL.

The act of pore solution, leaving water filled corrosion space in the binder, can be divided in acid dissociation, buffer capacity and solubility of salts, resp. their precipitation and dissolution. The ratio of C/S is decreasing due to blending the cement with admixtures, especially with SiO_2 rich admixtures like FA, and due to pozzolanic reaction. The neutralization capacity decreases with lower content of CH making the concrete more stable in acidic conditions.



Fig. 5 Rims of Fe hydroxides (upper image) and reflective Fe phases as buffer layer between corroded and uncorroded layer of PII concrete, silage effluent, 6 months, RL

The used aggregate consisting mostly of rounded particles of quartz was found to be relatively stable in environment of lower pH showing no signs of deterioration after 6 months of exposure. Quartz sand aggregate (SiO₂-rich) has very low neutralization capacity contrarily to limestone aggregate with $CO_3^{2^2}$.

On the boundary of corroded and uncorroded concrete, there is visible diffusion barrier of Fe-rich crystalline soluble salts. These phases are reflective in RF (**Fig. 5**) presented as brighter rims between corroded and uncorroded concrete. The result of degradation is visible in FL mostly as lighter porous surface layer. But in some cases, precipitation of Fe phases makes this corroded layer darker and less distinct.

The depth of corroded layer is difficult to analyze, since there is no continuous corroded layer on the surface. The depth and also the composition of corroded layer is dependent on type of cement, admixtures used and position of aggregates and can be affected by preparation, because the grindability of corrosion products or porous residue during preparation of thin section is easier than that of uncorroded concrete. Previous study showed that the depth of deterioration by acid was 2–4 times less for SiO₂-rich SCMs based concrete mainly due to lower Ca/Si ratio and less propagation of micro-cracks was observed for SCMs-based concrete attacked by sulfate [21]. The surface of the concrete stored in silage effluent is often covered with efflorescent. More calcite efflorescence are visible on concrete without admixtures (samples C and CII).

Strength development

Standard test bars of samples stored in aggressive media were tested after 12 and 20 months. Samples were compared to reference sample stored in distilled water (**Fig. 6, 7**).

Concrete produced only using CEM I 42.5R (i.e. mix design C) showed markedly the effect of biogenic sulfuric acid, which was less considerable when using CEM II 32.5 R. In case of samples stored in biogenic sulfuric acid, sample C (using CEM I 42.5R) compared to CII (CEM II 32.5 R) show considerably stronger deterioration after 12 and 20 months. Admixtures play an important role in terms of maintaining the strengths for samples stored in lactic acid, with better results for combination of slag and fly ash compared to fly ash cement. Samples with admixtures are more resistant to sulfuric acid showing better strengths compared to reference concrete. Generally, in acidic environment, all samples maintain better the flexural than compressive strengths. Previously it was reported that the compressive strength of PC samples was found to reduce by 21% after 12 months exposure to silage effluent [22]. Similar results in terms of compressive strengths were obtained in our study. Admixtures rich in Al₂O₃ can improve the resistance of concrete in aggressive solutions. Binders with higher Al content, whether it is concrete or geopolymer, are more intensely crosslinked and therefore more resistant to decalcification [22].



Fig. 6 Compressive and flexural strength comparison, % of reference sample, 12 months



Fig. 7 Compressive and flexural strength comparison, % of reference sample, 20 months

Conclusions

Calcite was detected in all samples as the reaction product. Bassanite, gibbsite, quartz, chrysoberyl and various salts and esters of lactic acid were reaction products of samples stored in lactic acid. Gypsum, ettringite, arcanite and quartz were formed in samples attacked by biogenic sulfur acid. Szomolnokite and quartz and were detected in samples stored in silage effluent. Brown calcite efflorescent forms a solid crust on concrete in silage effluent. In samples stored in lactic and acetic acid, calcite, quartz and sylvite was monitored. In case of silage effluent, the concentric rims structures of calcite efflorescence with various thickness was observed. Calcite crust is the product of carbonation of salts of lactate acid. White to yellowish white massive or tabular crystals of gypsum on the surface of samples stored in biogenic sulfur acid were present. Diffusion barrier rich in Fe between corroded and uncorroded concrete was observed in reflected light. Combination of slag and fly ash compared to fly ash cement was better in terms of maintaining the strengths for samples stored in lactic acid. Admixtures improved concrete resistance to sulfuric acid showing better strengths compared to reference concrete.

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