Analysis of biologically induced concrete deterioration in a wastewater plant by combining microstructural analysis with thermodynamic modeling

A. Leemann, B. Lothenbach, C. Hoffmann

Empa, Dübendorf, Switzerland

Abstract

In the nitrification basins of wastewater treatment plants, deterioration of the concrete surface can occur. The nitrifying biofilm covering the concrete oxidizes ammonium into nitrate and causes a decrease of pH resulting in an acid attack.

To identify the mechanism of deterioration, concrete cubes of different composition were suspended in a ventilated nitrification basin of a wastewater treatment plant. After two years of exposure, the cubes were removed.

The microstructural investigation reveals that not only leaching of paste and aggregates due to the acid attack takes place. Calcite precipitation close to the surface occurs due to the presence of bicarbonates in the attacking solution and leads to the formation of a dense layer. The degree of corrosion of the different cubes shows no correlation to concrete strength or oxygen diffusion of the unaffected core concrete but correlate with the CaO-content of the different cements used. Cements which contain a high fraction of CaO form more calcite and thus a denser layer offering a better protection against the acid attack. The presence of slag, which lowers the amount CaO in the cement, leads to a faster deterioration of the concrete than observed for samples produced with pure OPC.

1. Introduction

Biologically induced concrete deterioration can be observed in a variety of environments (e.g. Parker, 1945; Sand and Bock, 1991; Josza et al., 1996; Warscheid and Braams, 2000). One of them is wastewater transport and treatment. Attack in sewer pipes usually takes place due to H₂S production of sulphate reducing bacteria and the subsequent formation of sulphuric acid by sulphate oxidizing bacteria (e.g. Parker, 1945; Parker, 1951; Sand, 1987; Attal et al., 1992; Davis et al., 1998; Nica et al., 2000; Vincke et al., 2001). But concrete deterioration is not limited to the occurrence of biological processes involving sulphur. In wastewater treatment plants, where aerobic conditions prevail, deterioration of the concrete surface can be observed in ventilated nitrification basins. The bacteria present as suspension in the wastewater and as a biofilm on the concrete surface oxidize ammonium to form nitrate:

$$NH_3 + O_2 \rightarrow NO_2^- + 3 H^+ + 2e^-$$
 (1)

$$NO_2^- + H_2O \rightarrow NO_3^- + 2 H^+ + 2e^-$$
 (2)

The ammonia-oxidizing bacteria responsible for the nitrification in such wastewater are Nitrosomonas, Nitrobacter, Nitrospira and Nitrosococcus species (e.g. Juretschko et al., 1998; Aoi et al., 2000; Dionisi et al., 2002; You and Chen, 2008; Kocamemi and Çeçen, 2009). Due to proton formation (see equations 1 and 2), the reaction causes a decrease of pH (Sand, 1997; Okabe et al., 1999) leading to an acid attack on the biofilm covered

concrete surface. There are indications that the pH can decrease to a value of 5.3 (Kaltwasser, 1976). The biologically induced attack leads to an erosion of the concrete surface, which decreases the thickness of the concrete cover protecting the reinforcement and with it the durability of the structure. In addition, sand and gravel on the floor of the basins are often removed periodically, as pumps can be damaged by eroded concrete aggregates.

In an attack by slightly acid liquids or water undersaturated in calcium carbonate, hydration products of cementitious systems are dissolved in the order of portlandite, AFm, AFt, calcite and progressing C-S-H decalcification (Faucon et al., 1996; Faucon et al., 1997; Faucon et al., 1998). The transport of attacking solution and dissolved ions is a function of diffusion and the dissolution front progresses with the square root of time (Faucon et al., 1998; Mainguy et al., 2000; Haga et al, 2005a; Haga et al, 2005b). Consequently, the progress of the dissolution front slows down with time. There are several additional factors influencing its progress. Firstly, the formation and preservation of the silica-rich layer at the surface is crucial. When it is removed, the rate of dissolution increases to the initial level and total leaching is accelerated (Koelliker, 1983; Grube and Rechenberg, 1987a; Grube and Rechenber; 1987b). Secondly, the rate of dissolution is decreased with decreasing water-to-cement ratio (w/c) (Maltais et al., 2004; Kamali et al., 2008; Beddoe and Schmidt, 2009). Thirdly, the type of binder has an influence on the diffusion coefficient. Systems with slag or fly ash have shown more resistance to leaching than systems with ordinary Portland cement (Faucon et al., 1998; Wee at al., 2001; Kamali et al., 2008).

Numerous studies deal with nitrifying bacteria present in wastewater (e.g. Juretschko et al., 1998; Aoi et al., 2000; Dionisi et al., 2002). However, there is little knowledge on the microstructural and chemical consequences for concrete exposed to a nitrifying biofilm.

In this project, the mechanisms of concrete deterioration are studied by exposing concrete cubes of four different mixtures in a wastewater plant. Four different concrete mixtures were used. After an exposure of two years, the concrete cubes were recovered. The oxygen diffusion coefficient of the unaffected inner part of the cubes was measured. Degree of deterioration of the concrete surface was assessed by analyzing microstructure and chemical composition. The experimental data were completed by thermodynamic modeling of the changes induced in concretes by the presence of slightly acid solutions containing bicarbonates .

2. Materials and Methods

2.1 Experiments

Four cements with different composition were used to produce the concrete mixtures and cubes (dimensions of 200 x 200 x 200 mm; Table 1 and 2); CEM I contains up to 5% limestone filler, CEM II/A-LL up to 20% limestone filler, CEM II/A-S up to 20% slag and CEM III/B up to 80% slag. A water-to-cement ratio (w/c) of 0.50 was used. The concrete was produced with alluvial sand and gravel consisting of sandstone, limestone and minor amounts of igneous/metamorphic rocks (grain size distribution of 0-32 mm). The superplasticizer used was based on naphthalin sulphonate.

A waste water plant showing problems of concrete deterioration was selected to expose the cubes. Water hardness in the plant fluctuates between 17 and 22 °fH, while pH values are kept at 7, a value required to ensure the stability of the microorganisms. The cubes were immersed in a ventilated nitrification basin. They were suspended at a depth of 5.0 m (1.2 m above the floor) using outriggers. After two years, the exposure was terminated and the cubes were investigated in the laboratory.

type	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	K ₂ O	Na ₂ O	SO₃	CO ₂	Blaine	loss on ignition	density
	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[cm ² /g]	[%]	[kg/m³]
CEM I 42.5 N	62.8	19.7	4.6	2.8	1.9	0.98	0.16	3.1	1.5	2940	2.8	3.13
CEM II/A-LL 42.5 N	61.3	17.4	4.1	2.5	1.7	0.84	0.12	2.8	5.7	3850	7.5	3.07
CEM II/A-S 32.5 R	57.3	22.9	5.6	2.5	2.7	0.99	0.27	3.0	n.a.	3320	1.6	3.09
CEM III/B 32.5 N	47.8	31.6	9.6	1.7	4.9	0.60	0.30	2.8	0.6	5360	1.9	2.94

Table 1: Composition of the four cements (n.a. = not analyzed).

mixture	C-OPC	C-LS	C-SL-1	C-SL-2	
cement type	CEM I	CEM II/A-LL	CEM II/A-S	CEM III/B 32.5 R	
	42.5 N	42.5 N	32.5 R		
cement content [kg/m ³]	325	325	325	325	
aggregate 0/32 mm [kg/m ³]	1940	1935	1935	1920	
water [kg/m ³]	163	163	163	163	
superplasticizer [kg/m3]	3.25	3.25	3.25	3.25	
w/c	0.50	0.50	0.50	0.50	

Table 2: Mix design of the concrete.

Oxygen diffusion was determined on two cores (diameter of 100 mm, length of 20 mm) taken from the inner part of the cubes unaffected by acid attack. The cores were first dried at 50°C for seven days and then at 110°C for two days. On one side of the core an oxygen flow was applied and on the other side a nitrogen flow, both having identical pressure. The oxygen content in the nitrogen flow was measured until equilibrium was reached. Afterwards, the oxygen diffusion coefficient was calculated according to Lawrence (1984).

Cores of the surface (diameter of 50 mm) were used for the microstructural investigation. The samples were dried in an oven at 50° C for three days, impregnated with epoxy resin and polished. In a first step, the samples were studied with an optical microscope. A reconstruction of the position of the original surface was made possible as parts of it were not eroded and were preserved during sample preparation as well. At 10 different locations per cube, the different layers formed due to deterioration where

identified and their depth was measured perpendicular to the concrete surface. For further investigation of the samples, an environmental scanning electron microscope (ESEM-FEG XL30) was used. The carbon coated samples were studied in the high vacuum mode (2.0-6.0 10^{-6} Torr) with an accelerating voltage of 15 kV and a beam current of 275-280 μ A.

Layers of different porosity were defined. The software for segmentation of the phases was developed in Matlab. The pixel size of the images used for the analysis was 1.55 x $1.72 \ \mu m^2$. The porosity was analysed in bands with a width of 15.5 μm as a function of depth.

The chemical composition of the concrete's surface layers was determined with energy dispersive X-ray spectroscopy (EDX). An EDAX 194 UTW detector, a Philips digital controller and Genesis Spectrum Software (Version 4.6.1) with ZAF corrections were used. In each layer ten area scans (about 20 x 20 μ m²) of the "outer product" were made to analyze its chemical composition.

2.2 Thermodynamic modeling

Thermodynamic modeling was used to study the chemical changes associated with the ingress of carbonate containing solutions in the different cement types. Thermodynamic modeling was carried out using the Gibbs free energy minimization program GEMS [27]. GEMS is a broad-purpose geochemical modeling code which computes equilibrium phase assemblage and speciation in a complex chemical system from its total bulk elemental composition. Chemical interactions involving solids, solid solutions, and aqueous electrolytes are considered simultaneously. The speciation of the dissolved species as well as the kind and amount of solids precipitated are calculated.

The thermodynamic data for aqueous species as well as for many solids were taken from the PSI-GEMS thermodynamic database [28, 29]. Solubility products for cement minerals including ettringite, different AFm phases, hydrogarnet, C-S-H and hydrotalcite were taken from the recent cemdata07 compilation [30]. For C-S-H an ideal solid solution between a jennite and a tobermorite type C-S-H was considered, but no solid solution between tobermorite and amorphous SiO₂. For the calculations it was assumed that all of the Portland cement had reacted, but only 50% of the slag (85 mass %) present in the CEMIII/B. A significant fraction of the slag is expected to remain unhydrated. Escalante et al. (2001) found a degree of reacrtion of 20 - 50% for slag blended with OPC, depending on hydration temperature, w/b ratio and replacement level. Lumley et al. (1996) reported for slags blended with Portland cements degrees of hydration between 30-55% after 28 days and 45-75% after 1-2 years. In the calculations the dissolution of amorphous SiO₂ gel was prevented as its dissolution kinetics is very slow at neutral and slightly alkaline pH conditions (Bickmore et al., 2006; Dove, 1994).

As the composition of the interacting solution in a waste water treatment plant can vary over time it was simplified. The presence of totally 2 mmol/l CO_3^{2-} was taken into account, corresponding to the 20 fH° reported in the waste water treatment plant. The carbonate was assumed be present as 0.67 mmol/l CaCO₃ and 1.33 mmol/l H₂CO₃ to be consistent with a pH value of 7.

Thermodynamic modeling can be used to calculate the changes associated with the ingress of carbonate or acid in a concrete sample. The ingress of carbonates can be mimicked in these calculations assuming that the core of the sample is in contact with no additional solution containing carbonates, while the area near the surface is in

contact with large quantities of solution. Even though these calculations do not relate directly to time and space, it is a convenient way to calculate the different conditions that a concrete sample submersed in carbonate solutions experiences. Such a modeling approach has the advantage that the calculations are very fast and flexible as no transport equations have to be considered, but has the disadvantage that the calculated data relate neither to time nor to distance.

3. Results

3.1 Oxygen diffusion coefficient

The oxygen diffusion coefficient of the different concrete mixtures varies significantly. Concrete C-SL-2 with slag shows the lowest value and concrete C-LS with limestone the highest (Table 3).

concrete	C-OPC	C-LS	C-SL-1	C-SL-2
O2-diffusion coefficient [10 ⁻⁸ m ² /s]	1.10	1.68	0.82	0.38

Table 3: Oxygen diffusion of the four concrete mixtures.

3.2 Porosity

Qualitatively, all four concrete mixtures show the same distribution of porosity close to the surface (Figure 1). There is a transition from the unaltered paste to a layer of increased porosity with a thickness between 100-800 μ m. The subsequent layer is very dense and only between 10 and 40 μ m thick. Finally, there is a layer of high porosity with a thickness between 100 and 700 μ m at the surface of the concrete. The segmentation of the images and their quantitative analysis show these differences in porosity more clearly (Figure 2 and 3). According to the differences in porosity, four layers can be identified:

- layer C: core, unaltered paste
- layer IP: inner layer with increased porosity compared to the unaltered paste
- layer HD: thin layer with high density
- layer OP: outer leached layer at the surface of the concrete with high porosity

The distance of these layers to the original uncorroded surface varies depending on concrete composition (Table 4).



Figure 1: Cut perpendicular to the surface of concrete C-OPC. Length of image: 2.5 mm. Backscattering electron image.



Figure 2: Segmentation into three classes: aggregates (light grey), paste (dark grey) and pores (black).



Figure 3: Porosity distribution of the paste at the surface of concrete C-OPC as analyzed from Figures 1 and 2.

concrete	C-OPC	C-LS	C-SL-1	C-SL-2
depth layer C [mm]	> 1.90	> 1.55	> 1.80	> 2.90
depth layer IP [mm]	1.05-1.90	1.00-1.55	1.2-1.80	1.45-2.90
depth layer HD [mm]	1.00-1.05	0.95-1.00	1.15-1.20	1.40-1.45
depth layer OP [mm]	< 1.00	< 0.95	< 1.15	< 1.40
porosity layer C [%]	16	20	19	18
porosity layer IP [%]	39	35	43	30
porosity layer HD [%]	8	6	9	12
porosity layer OP [%]	73	80	83	79

Table 4: Mean values for depth and porosity of the surface layers.

3.3 Chemical composition

The depth profiles of chemical composition are directly related to the ones of porosity and are very similar for all concrete mixtures. Layer IP shows a depletion of Ca compared to the unaltered paste. Apparently, it is leached from portlandite and C-S-H. The Ca concentration in the paste decreases from 55 % to 40 % in layer IP. The main component of layer HD is Ca that is present as newly formed calcite aggregations with a diameter of several micrometers and as finely dispersed calcite in the sub-micrometer range. Its Ca concentration shows variations between 63 % (C-SL-2) and 70 % (C-OPC). Layer OP at the surface of concrete is even more depleted in Ca than layer IP (Figure 4). The Ca concentrations vary between 16 % (C-OPC) and 28 % (C-LS). Si is the main component with concentrations ranging from 39 % (C-LS) to 55 % (C-OPC). In general, sulphur content decreases approaching the surface, while the relative fractions of Al and Fe increase. The chemical gradients of Ca, S, Fe and Al are best shown in comparison with Si (Figure 4 and 5).



Figure 4: Atomic ratio of Ca/Si present in the different layers. Mean values of the four concrete mixtures.



Figure 5: Atomic ratio of S/Si, Fe/Si and Al/Si present in the different layers. Mean values of the four concrete mixtures.

3.4 Thermodynamic modeling

Thermodynamic modeling was used to calculate the changes associated in the different concretes in the presence of a solution with a water hardness of approx. 20 fH $^{\circ}$ and a pH of 7. In the calculations, only the interaction of the solution with the cement paste was considered, while no interaction with the aggregate was assumed.

The unaffected core of concrete C-OPC is calculated to consist mainly of C-S-H, portlandite, ettringite and monocarbonate, with smaller quantities of calcite, hydrotalcite, and hemicarbonate (Figure 6a). Upon the ingress of H_2CO_3 and CaCO₃ solution, the calculations predict that first portlandite becomes unstable and the Ca/Si ratio of the C-S-H starts to decrease (Figure 6a). Eventually also the monocarbonate and ettringite become unstable forming calcite and small quantities of strätlingite. This leads to an inner zone which is leached with respect to calcium and sulfate. Nearer to the surface also the remaining C-S-H is leached to form calcite and amorphous silica gel. The carbonate (and calcium) of the ingressing solution leads to the formation of a

calcite layer in a zone where a calculated pH in the range of 8 to 12 is present. Additional calcium to form calcite is also leached from monocarbonate, ettringite and the C-S-H phase (Fig 6). The formation of such a calcite layer fills up a significant portion of the available pore space. At the surface calcite is unstable relative to the surrounding solution, while amorphous SiO₂, Al(OH)₃ and Fe(OH)₃ gel will persist. Note that the dissolution of amorphous SiO₂ gel was suppressed in the thermodynamic calculations as its dissolution kinetics is very slow at near neutral pH conditions. The outermost layer is depleted with respect to Ca and has a low degree of space filling (Figure 7a and b). The calculated sequence of different layers agrees with the experimental observations in this study (see above Fig 1-3) and also with the experimentally observed formation of a dense calcite layer in oilwell cements exposed to solutions containing calcium and carbonates (Neuville et al., 2008; Duguid et al., 2007).

The influence of H₂CO₃ and CaCO₃ solution on concrete C-LS is similar. The main difference to concrete C-OPC is the presence of additional calcite, which leads to slight dilution of Portland cement (Figure 6b). The core region of concrete C-SL-2, which may contain up to 80% slag is calculated to consist of C-S-H (with a Ca/Si ratio of ~1.5), hydrotalcite, strätlingite and small amounts of monosulfate, mono- and hemicarbonate. The calculated changes associated with the ingress of calcium and carbonate-containing solutions are similar to the changes in the other cements. Near the unaffected core, monocarbonate and ettringite become unstable with respect to calcite and strätlingite. Nearer to the surface, C-S-H and strätlingite convert to calcite, SiO₂ and Al(OH)₃. Significantly less calcite is calculated to be formed in concrete C-SL-2, as in its paste much less calcium is available which can react with carbonate to calcite (Figure 6c). This leads to a smaller reduction of porosity in the calcite layer (Figure 7b) and to lower buffer capacity against ingressing protons as indicated by the lower pH values in the presence of concrete C-SL-2 (Figure 7c).





Figure 6: Calculated changes in the hydrate assemblage of a) concrete C-OPC (CEM I), b) concrete C-LS (CEM II/A-LL) and c) concrete C-SL-2 (CEM III/B) upon the ingress of a solution containing 0.67 mM CaCO₃ and 1.33 mM H₂CO₃. A complete reaction of the Portland cement clinker and a reaction degree of 50% of the slag in CEM III/B is assumed.



Figure 7: Calculation for concretes C-OPC (CEM I), C-LS (CEM II/A-LL) and C-SL-2 (CEM III/B) a) total porosity of the concrete, b) molar Ca/Si ratio in the paste and c) pH in the pore solution upon the ingress of a solution containing 0.67 mM CaCO₃ and 1.33 mM H_2CO_3 .

4. Discussion

The differences in oxygen diffusion between the different concrete mixtures are caused by the different cements, as w/c is identical. The presence of limestone powder as in concrete C-LS can increase porosity and permeability (Table 4; Tsivilis et al., 1999; Tsivilis et al., 2003; Matschei et al., 2007). In contrast, the use of slag as in concrete C-SL-1 and C-SL-2 lowers permeability (Table 4; Chang et al., 2005; Loser et al., 2009).

The changes in porosity observed in the different layers are caused by dissolution and precipitation of minerals. With progressing deterioration, portlandite is leached and C-S-H is decalcified as shown by the changes in Ca/Si-ratio (layers IP and OP). The depletion of calcium at the concrete surface clearly indicates that the concrete corrodes due to an acid attack. However, the slow progress of deterioration indicates an only slightly acidic environment. The precipitation of calcite leading to the formation of layer HD occurs when the Ca ions react with the bicarbonate that is present in the attacking solution (Figure 6; Neuville et al., 2008). The resulting formation of dense layer HD slows down further deterioration not only due to its low porosity but also because it acts as a buffer for intruding protons (Pfingsten, 2002). The formation of a protective calcite layer has been observed in the presence of solutions containing calcium carbonates in oil well cements in the temperature range from 20 to 80 °C (Duguid et al., 2007; Neuville et al, 2008). Furthermore, the formation of the surface layers increase the distance from the surface to the unaltered paste. Together with the low porosity of layer HD and its buffer capacity, they slow down the acid attack considerably. However, due to the high porosity of layer IP and OP, these surface layers exhibit low strength and may be easily removed by mechanical cleaning. Once the surface layers are removed, dissolution is increased again leading to a higher degree of deterioration (Grube and Rechenberg, 1987a; Grube and Rechenberg, 1987b; Leemann et al., 2009). Apart from calcium, the corroded zones are depleted in sulphur agreeing with the results obtained by leaching experiments of pastes with pure water (Faucon et al., 1998; Moranville et al., 2004).

The depth of layer HD indicates how far the biodeterioration has progressed into the concrete. Therefore, it can be used as a measure for the degree of biodeterioration (Leemann et al., 2009).

The deterioration degree of the exposed cubes does not decrease with decreasing oxygen diffusion coefficient (Figure 8) or with decreasing porosity of the unaffected core (Table 4). In fact, deterioration and oxygen diffusion coefficients of the unaltered concrete show an opposite trend. Even if concrete deterioration in the wastewater plant is a diffusion process, the initial diffusion coefficient is clearly not the governing parameter under the prevailing conditions. The comparison between the depth of layer HD and CaO-content of the cements used for the different concrete mixtures uncovers that the latter is the main parameter controlling the process (Figure 9). When the biofilm produces the same amount of protons on the surface of the different mixtures, the buffer capacity of the individual concrete determines the volume of paste needed for neutralization or in other words the depth of deterioration. In addition, the presence of more CaO will lead to formation of more calcite resulting in stronger reduction of porosity, which might even results in a complete blocking of the porosity as reported by Pfingsten et al. [19]. Even if this layer is generally thin, it will slow down diffusion. As the amount of CaO in the slag cements is lower than in OPC and cement with limestone

powder, concrete C-SL-2 is affected the most and concrete C-OPC and C-LS the least. When a dense calcite layer is formed, it protects the concrete due to a decrease in diffusivity and due to its buffer capacity.

Diffusivity or permeability in the three degraded outer layers could not be determined experimentally. However, the diffusivity in cementitious materials depends on their porosity (e.g. Garboczi and Bentz, 1992; Bentz and Garboczi, 1992). As an example, the porosity determined for concrete C-OPC (Table 4) can be used to determine relative diffusivity of the different surface layers according to Garboczi and Bentz (1992). The determined values for layer HD are about 400 times lower than for layer OP and 70 times lower than for layer IP. Thus, even tough the layer HP is very thin, the transport of ions in the surface layers is slowed down significantly because of the formation of calcite in the layer HD.

The observed resistance of the different concrete mixtures does not agree with numerous leaching experiments or with the resistance of concrete against strong acids that shows a higher resistance for systems with slag or fly ash compared to ordinary Portland cement systems (Faucon et al., 1998; Wee et al., 2001; Chang et al., 2005; Bassuoni and Nehdi, 2007; Kamali et al., 2008; Beddoe and Schmidt, 2009; Gruyaert et al., 2009). In these cases, the disagreement can be mainly attributed to differences in the test set-up and the absence of carbonates in the attacking solution.

However, not only cement composition has to be taken into account assessing the deterioration resistance of concrete. Aggregate containing calcite should increase the buffer capacity of the concrete (Chang et al., 2005; Duguid et al., 2007). Especially the composition of the fines can be expected to be important due to their high surface area. A decrease of w/c can increase the resistance of the concrete (Maltais et al., 2004; Kamali et al., 2008; Beddoe and Schmidt, 2009). The decrease of initial concrete diffusivity seems of minor importance in the present case. a decrease leads to a higher density of the paste with an increase of CaO-content per volume that should improve the buffer capacity of the concrete.



Figure 8: Depth of calcite layer on untouched side versus oxygen diffusion coefficient.



Figure 9: Depth of calcite layer on untouched side versus CaO content of the cements used for concrete production.

5. Conclusions

Concrete exposed in a ventilated nitrification basin of a wastewater plant can be corroded due to proton production of a nitrifying biofilm covering it surface.

The deterioration caused in the acidic environment leads to specific microstructural features if significant quantities of bicarbonates are present in the water:

- layer OP: outer, highly porous layer depleted in calcium at the concrete surface
- layer HD: dense, calcite rich layer
- layer IP: layer with increased porosity compared to unaltered paste
- layer C: unaltered paste

These layers reduce the progress of deterioration as they increase the distance between biofilm/surface and unaltered paste. Furthermore, layer HD slows down diffusion and acts as a buffer due to its low porosity and high calcite content.

The removal of these protective layers as often done in practice during cleaning accelerates deterioration.

The results of thermodynamic modeling show a good agreement with the experimental results and explain the observed profiles of porosity and chemical composition. Under the prevailing conditions, the degree of deterioration is not dependent on the diffusion coefficient of the unaltered concrete but on the CaO-content of the cement used in the concrete. The presence of slag or other supplementary cementitious materials rich in Si and poor in Ca, such as microsilica or slag, lowers the capacity to form calcite upon the ingress of carbonate containing solutions. If less calcite is formed, the porosity of the calcite rich layer HD is higher and in addition the buffer capacity against protons is lowered. All these factors are expected to lower the resistance of cements with silicon rich mineral admixtures as slag against solutions containing both protons and carbonates.

Aggregates may also contribute to the buffer capacity of the concrete, if they contain significant amounts of limestone.

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