

# Concrete erosion in nitrification basins of wastewater treatment plants

Andreas Leemann<sup>1</sup>, Cathleen Hoffmann<sup>2</sup>

ABSTRACT: Recently erosion of the concrete surface in nitrification basins of wastewater treatment plants (WWTP) has been observed. The degree of erosion varies between different WWTP. The cause of the erosion and the reasons for these variations are not clear. In this study, concrete samples have been produced with different cement types (ordinary Portland cement, ordinary Portland cement blended with limestone powder, ordinary Portland cement blended with slag). After curing, the samples were exposed in the nitrification basins of four WWTP with different water hardness during 282 days. The erosion rate was measured every three month. At the end of the exposure period, the microstructure of the samples was analyzed with SEM.

The nitrifying biofilm on the concrete surface triggers an acid attack. With progressing attack, portlandite is leached and CSH is decalcified. However, the precipitation of calcite and the resulting formation of a dense calcite layer close to the concrete surface slow down erosion propagation. The erosion rate in the WWTP is influenced by cement type, w/c and water hardness. Based on the experimental results, the importance of the different parameters can be specified with water hardness being the most dominant one.

# 1 INTRODUCTION

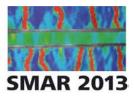
Chemical attack on concrete is present in a variety of environments. In the transport and treatment of wastewater, the most common form is an attack by sulphuric acid triggered by the the reduction and ensuing oxidation of sulfur by bacteria in sewage pipes (Parker, 1945 / Attal et al., 1992). Recently, erosion of the concrete surface in nitrification basins of wastewater treatment plants (WWTP) has been observed (Figure 1). In such aerated tanks, the oxidation of ammonium to nitrate by bacteria may be linked to a pH decrease (Sand, 1997 / Okabe et al., 1999). The ammonium is oxidized in two steps (equs. 1 and 2) to nitrate In the first step, ammonia is oxidized to nitrite by ammonia oxidizer; the nitrite is then oxidized to nitrate by nitrite oxidizer by autotrophic nitrifiying bacteria belonging to Nitrosomonas, Nitrobacter, Nitrospira and Nitrosococcus species (e.g. Juretschko et al., 1998, Guyer, 2010).:

$$NH_3 + 1.5 O_2 \rightarrow NO_2^- + H_2O + H^+$$
 (1)

$$NO_2^- + 0.5 O_2 \rightarrow NO_3^-$$
 (2)

<sup>&</sup>lt;sup>1</sup> Empa - Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland

<sup>&</sup>lt;sup>2</sup> Holcim (Schweiz) AG, Würenlingen, Switzerland



$$NH_3 + 2.0 O_2 \rightarrow NO_3^- + H_2O + H^+$$
 (1+2)

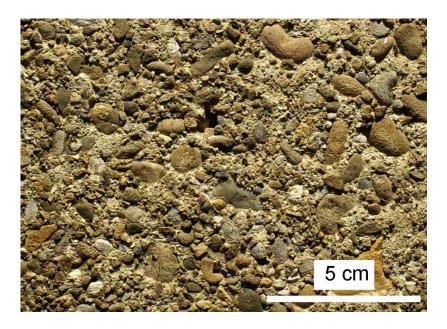


Figure 1: Eroded concrete surface in WWTP.

To ensure the stability of the bio-organisms, the pH of the water in the basins is kept at a neutral value of 7. But as the concrete surface in such basins is covered by a nitrifying biofilm, an acidic environment between biofilm and concrete surface can be established leading to an acid attack. The erosion of the concrete surface possibly decreases the durability of the structure as the thickness of the concrete cover protecting the reinforcement is reduced. The degree of concrete erosion varies widely between different WWTP in Switzerland, but the reasons for these variations are not clear.

The goal of this project is the identification and assessment of the mechanism leading to the biologically triggered concrete erosion in WWTP. Additionally, the variations in the degree of erosion between different WWTP are investigated. Four different WWTP were selected to expose concrete specimens in their nitrification basin to study kinetics of erosion, influence of cement type, water-to-cement-ratio (w/c) and water hardness.

# 2 MATERIALS AND METHODS

The cements used and the mix design of the concrete are given in Table 1. Alluvial gravel consisting mainly of sandstone and limestone with a maximum grain size of 32 mm was used as aggregate.

Prisms with a size of 72 X 72 X 150 mm<sup>3</sup> were cut from the previously produced concrete cubes. A calibrated depth gauge combined with a steel plate having angles and 20 predrilled holes ensured that surface erosion was always measured at identical points. The repeatability of the method as tested is about 0.02 mm.

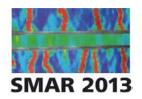


Table 1: Mix design of the concrete. The names of the concrete mixtures given in row 1 of column 2 correspond to the order of cements given in row 2 of column 2 (CEM I 42.5 = ordinary Portland cement, CEM II/A-LL = Portland limestone cement, CEM III/B = Portland slag cement).

mixtures	C-OPC-1, C-LS, C-SL	C-OPC-2
cement types	CEM I 42.5 N, CEM II/A-LL 42.5 N,	CEM I 42.5 N
	CEM III/B 32.5 R	
cement content [kg/m <sup>3</sup> ]	325	375
aggregate 0/32 mm	1935	1940
[kg/m <sup>3</sup> ]		
water [kg/m <sup>3</sup> ]	163	150
superplasticizer [kg/m <sup>3</sup> ]	-	5.6
w/c	0.50	0.40

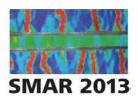
The first set of specimens was exposed in four different WWTP (A-D) after air curing at 20°C and 70% relative humidity for 28 days, the second set after water curing at 20°C for 90 days. The range of water hardness of the different WWTP is 19.5-32.0 fH°. Every three month, the measured surfaces were cleaned with a soft brush and erosion was measured up to an age of 282 days. Afterwards, the specimens were removed from the WWTP for microstructural analysis. After drying, impregnation with epoxy resin, polishing and coating the samples, they were analyzed with a scanning electron microscope (ESEM-FEG XL30) in the high-vacuum mode.

# 3 RESULTS

After an exposure of 282 days the surface area of the different mixtures shows the same microstructure in all samples. Four different zones can be distinguished based on their porosity (Figures 2):

- zone OP: highly porous layer at the concrete surface (thickness: 0.3-0.6 mm)
- zone HD: dense layer (thickness: 0.01-0.02 mm)
- zone IP: layer with increased porosity compared to unaltered concrete (thickness: 0.7-1.3 mm)
- zone C: unaltered paste

The defined zones show differences in composition and porosity. The differences mainly relate to the Ca/Si-ratio (Figures 3). Zone OP is depleted in calcium as a result of portlandite  $(Ca(OH)_2)$  dissolution and decalcification of the main hydration product calcium-silicate-hydrate (C-S-H). The high density in zone HD is due to calcite precipitation. Calcium leaching in zone IP leads to a relatively low Ca/Si-ratio compared to the unaffected core (zone C).



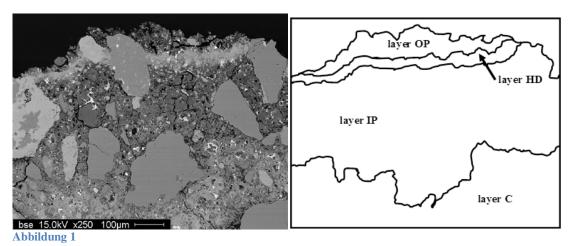


Figure 2: Surface area of concrete C-OPC-2 with unaffected core (zone C), inner porous layer (zone IP), dense calcite layer (zone HD) and outer porous layer (zone OP).

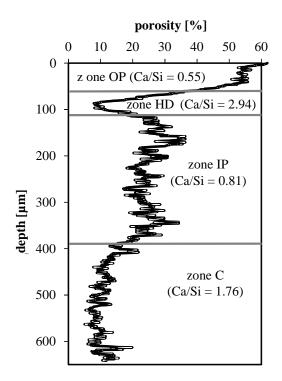
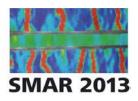


Figure 3: Relative porosity and the average molar Ca/Si-ratio (number in of the hydrates in the different layers (see Figure 2) of concrete C-OPC-2.

The sequence of concrete composition in regard to erosion rate is the same in all WWTP. Concrete C-LS has the highest resistance towards erosion and and concrete C-SL the lowest (Figure 4). The reduction of w/c-ratio in the case of concrete C-OPC slows down erosion.

There are substantial differences in concrete erosion between the different WWTP (Figure 5). The specimens with a curing time of 90 days in water show slightly lower erosion than specimens air cured for 28 days.



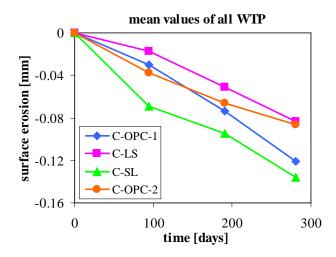


Figure 4: Surface erosion of the different concrete mixtures. Mean values for all WWTP.

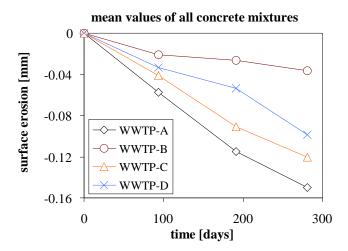
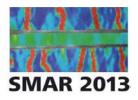


Figure 5: Surface erosion in the different WWTP. Mean values for all concrete mixtures.

#### 4 DISCUSSION

Portlandite is leached and C-S-H is decalcified with progressing erosion, as it is shown by the changes in Ca/Si-ratio of the different zones. The erosion rate is influenced by the CaO content of the cement as the buffer capacity increases with increasing CaO content. The precipitation of calcite and the resulting formation of a dense calcite layer (zone HD) influence erosion propagation. Calcite is precipitated when the dissolved calcium ions react with the bicarbonate that is present in the attacking solution. The calcite precipitated has a sealing effect on the surface of the concrete. This efficiently slows down further attack (Pfingsten, 2002). Calcite formation increases with water hardness and erosion rate decreases. The leached zones are of low strength due to their high porosity. If these protective zones are removed by a cleaning of the concrete surface, concrete erosion will accelerate. Therefore, cleaning should be avoided (Grube & Rechenberg, 1987 / Leemann et al., 2009).



The concrete surfaces that are cleaned four times per year show yearly erosion rates between 0.02 and 0.30 mm in the four WWTP. The resistance of the concrete surface to erosion increases with good curing. Due to the formation of protective layers, erosion of uncleaned concrete surfaces is a nonlinear process showing a decrease with age. Therefore, the experimentally determined erosion rates can be expected to be lower with longer intervals for cleaning. Typical intervals for rehabilitation are 25 years long. In this time span concrete erosion is not expected to lead to a decreased durability of the structures.

The importance of the different parameters can be specified based on the experimental results. Water hardness is the most dominant one (Figure 6).

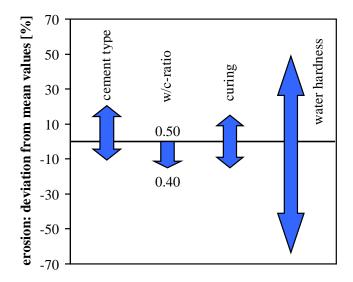


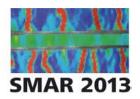
Figure 6: Influence of cement type, w/c and water hardness based on the experimental results.

# 5 SUMMARY AND CONCLUSIONS

Biodeterioration causes the erosion of the concrete surface in nitrification basins of WWTP. Acid in form of carbon dioxide is produced in the nitrifying biofilm and the surface of the concrete leading to the dissolution of hydration products (e.g. Ca(OH)<sub>2</sub>) and the ensuing erosion. The progress of erosion is significantly influenced by the formation of different layers (layers OP, HD and IP) below the concrete surface increasing the distance to the unaltered concrete. In particular, the dense calcite layer HD decreases diffusivity and acts as a buffer leading to an improved resistance. The removal of these layers by cleaning therefore accelerates concrete deterioration.

All studied concrete mixtures show a degree of surface erosion, but its extent depends on different parameters:

- The use of cement with a high CaO content is beneficial as it increases the buffer capacity of the concrete.
- The density of the concrete is increased by a reduction of w/c, leading to a decreased permeability, a higher CaO content per volume and with it to an increased buffer capacity.
- Good curing optimizes cement hydration and causes a denser, less permeable microstructure. Moreover, more hydration products to neutralize protons are readily available.



- Water hardness is the dominating factor for the progress of the erosion as it acts as a buffer slowing down the dissolution of the concrete and the diffusion of the calcite layer into the concrete. Additionally, it facilitates calcite precipitation increasing the density of the calcite layer and with it additionally slowing down acid transport into the unaffected concrete.
- The measured surface erosion rates in the nitrification basins of the studied WWTP are only fractions of a millimeter per year and appear to be no danger for the durability of the structures within the expected lifetime of a WWTP.

# 6 ACKNOWLEDGEMENT

cemsuisse is acknowledged for the financial support of the project.

#### 7 REFERENCES

- Attal, A, Brigodiot, M, Camacho, P, Manem, J. 1992. Biological mechanisms of H<sub>2</sub>S formation in sewer pipes. *Water Science & Technology*, 26: 907-914.
- Grube, H, Rechenberg, W. 1987. Betonabtrag durch chemisch angreifende saure Wässer. *Beton*, 11: 446-451.
- Juretschko, S, Timmermann, G, Schmid, M, Schleiffer, KH, Pommerening-Röser, A, Koops, HP, Wagner, M. 1998. Combined molecular and conventional analysis of nitrifying bacterium diversity in activated sludge: Nitrosococcus mobilis and Nitrospira-like bacteria as dominant populations. *Applied and Environmental Microbiology*, 64: 3042-3051.
- Gujer, W, 2010. Nitrification and me. A subjective review. Water Research, 44:1-19.
- Leemann, A, Lothenbach, B, Hoffmann, C, Bischof, S, Lunk, P. 2009. Concrete corrosion in a wastewater plant. In: Concrete in Aggressive Aqueous environments, Alexander, MG, Bertron, A (Eds). Proc Inter RILEM TC 211-PAE Final Conf, Toulouse: 116-124.
- Okabe, S, Satoh, H, Watanbe, Y. 1999. In situ analysis of nitrifying biofilm as determined by in situ hybridization and the use of microelectrodes. *Applied Environmental Microbiology*, 65: 3182-3191.
- Parker, C. 1945. The corrosion of concrete. Isolation of a species of bacterium associated with the corrosion of concrete exposed to atmospheres containing hydrogen sulphide. *Australian Journal of Experimental Biology and Medical Sciences*, 23: 14-17.
- Pfingsten, W. 2002. Experimental and modeling indications for self-sealing of cementitious low- and intermediate-level waste repository by calcite precipitation. *Nuclear Technology*, 140: 63-82.
- Sand, W. 1997. Microbiological mechanisms of deterioration of inorganic substrates a general mechanistic overview. *International Biodeterioration and Biodegradation*, 40: 183-190.