Slurry acidification

Micro-structural analysis of concrete after exposure to acidified and non-acidified slurry

Lena Rodhe, Mariusz Kalinowski,
Leticia Pizzul, Johnny Ascue,
Marianne Tersmeden

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Baltic Slurry Acidification

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Preface

Baltic Slurry Acidification is a flagship project in the action plan for EU strategy for the Baltic Sea Region (BSR). The project is being carried out between 2016-2019 with a budget of 5.2 million euros, of which 4 million euros is funded by the EU Regional Development Fund through the Interreg Baltic Sea Region Program.

The general aims of the project are to reduce ammonia emissions from animal production and create a more competitive and sustainable farming sector by promoting the implementation of slurry acidification techniques (SATs) throughout the Baltic Sea Region. This report falls under Work Package 2 – Technical feasibility studies, which aims to identify technical issues, bottlenecks and other barriers to the implementation of SATs, originally developed in Denmark, to other countries in the BSR.

This report is from Activity 2.2 ‘Equipment quality evaluations’. The work has been carried out by Partner RISE in Sweden. Senior Researcher Lena Rodhe led the work and is the main author. The experiment was conducted by a team consisting of laboratory engineer Johnny Ascue, technician Marianne Tersmeden and researcher Leticia Pizzul. The structural analysis of the concrete samples was planned and performed by Senior Researcher Mariusz Kalinowski at RISE CBI Betonginstitutet.

We are very thankful to Jan Lillieblad and Anders Olofsson, both at Abetong AB, who very kindly supported us with their expertise and concrete samples of different qualities. Without their help it would have been hard to perform these studies.

28 February 2019

Erik Sindhöj
Project Coordinator for Baltic Slurry Acidification

Summary

Samples of three different concrete qualities were prepared and hardened, before exposure to cattle slurry without sulphuric acid (A) and with sulphuric acid added until pH<5.5 (B). The samples were exposed for two years in containers with about 45 L slurry. The boxes with slurry and concrete samples were placed in a ventilated room at 20 °C. The slurry and air temperatures were recorded continuously with temperature loggers, data being recorded every third hour. The slurry level in the boxes and the slurry pH were checked regularly during the experiment. Slurry or acid was added, if necessary, to maintain the level and pH<5.5. Before pH measurements, the slurry was stirred gently in both boxes. To restrict evaporation, the containers had non-airtight plastic covers between measurements.

Half-way through exposure, the old slurry was replaced with fresh slurry (acidified and non-acidified treatments) to mimic conditions in farm storage where fresh slurry is added continuously during storage. After two years' storage, the experiment was finalised. The concrete samples were taken out of the slurry, washed gently with water and put into labelled plastic bags.

The samples were delivered to RISE CBI's concrete laboratory, where the structural analyses were performed. These used petrographic microscopy techniques to examine the effects of exposure to two potentially aggressive environments, non-acidified and acidified cattle slurry, on concrete with three different mixes. The studied surfaces in the concrete samples were oriented vertically in the plastic containers. Polished sections were evaluated with a stereo microscope, and thin sections were evaluated using a polarising microscope and sources for visible and UV light.

The results of the study show that the acidified slurry is more chemically aggressive to the cement paste in all the concrete mixes analysed. This can be explained by the solution's lower pH.

The extent of the chemical attack correlates with the initial quality of the concrete mix (water-powder ratio and type of binder). The deepest chemical attacks were observed in samples A1 and B1 consisting of "regular" concrete mix with w/c 0.59. The "long lasting quality" (LLC) concrete with a binder specially developed for low-pH environments shows markedly better resistance to chemical attack.

The effects of the chemical attack on concrete after two years' exposure can be classified as weak, consisting mainly of an increase in the capillary porosity of the cement paste in the outer layer of the concrete. The increase in porosity is considered to be due to the partial leaching of calcium hydroxide.

Introduction

Aim

The aim of the study was to see the impact of acidified slurry on different concrete qualities during long-term exposure, and to formulate recommendations for the concrete quality to use when implementing acidification of slurry on the farm level.

Material and methods

Treatments

Three qualities of concrete manufactured by the company ABetong were tested (Table 1). Samples consisted of concrete cubes (0.1 m x 0.1 m x 0.1 m) tested in duplicates. The samples were hardened for 28 days in water, before exposure to cattle slurry with and without sulphuric acid added. Samples were exposed for two years.

Table 1. Number of samples of three qualities exposed in two slurry types, with and without sulphuric acid. Two replicates of each concrete sample were used for each combination

	Slurry type	
Concrete quality	A) Cattle slurry, no acid	B) Cattle slurry, acid, pH<5.5
1) w/c m 0.59, (quality of ground plate of liquid storage)	2	2
2) w/c m 0.48, (quality of wall element of storage)	2	2
3) Long Life Concrete quality (LLC), used in silage storages	2	2

w/c m, water–cement ratio is the ratio of the weight of water to the weight of cement used in a concrete mix.

LLC, product from ABetong, especially developed for low-pH material like silage.

Slurry

The concrete samples were exposed in cattle slurry without (A) and with acid added (B). The cattle slurry was taken from the pumping pit (fresh slurry) on a dairy farm (Table 2). The cattle slurry was divided into two parts. One was acidified to pH<5.5 by slowly adding concentrated sulphuric acid with gentle manual stirring, while the other had no acid added, but was also stirred in similar way. The process was repeated for about two weeks until the pH was stabilised. After preparation, slurry samples were taken from each slurry type to be analysed for nutrient content including sulphur.

After pH stabilisation, the concrete samples were 2 December 2016 put into the slurry to be exposed for about two years. The pH was checked regularly after the slurry had been stirred, and additional diluted acid 1:4 (acid:water by volume) was added if necessary. The container with non-acidified slurry was stirred in the same way and as many times as the acidified slurry to make similar conditions for the two slurry types. After less than one year (4 October 2017) new slurry was prepared and the concrete samples were transferred to the new slurry that had been treated as before. The total amount of acid added was calculated for the first and second periods. The exposure of the samples stopped on 6 November 2018, after nearly two years.

Experimental set up

The samples were placed at least 0.1 m apart, on strips of wood in two containers, one for each slurry type, to expose the samples from all sides (Figure 1). The two types of slurry were added to the containers, respectively, to a depth of about 0.17 m, ensuring the samples were covered with a layer of slurry about 0.03 m thick. The boxes were placed in a ventilated room at 20 °C, where the concrete samples were exposed for almost two years (Figure 2).

To restrict evaporation, the containers had non-airtight plastic covers between measurements.

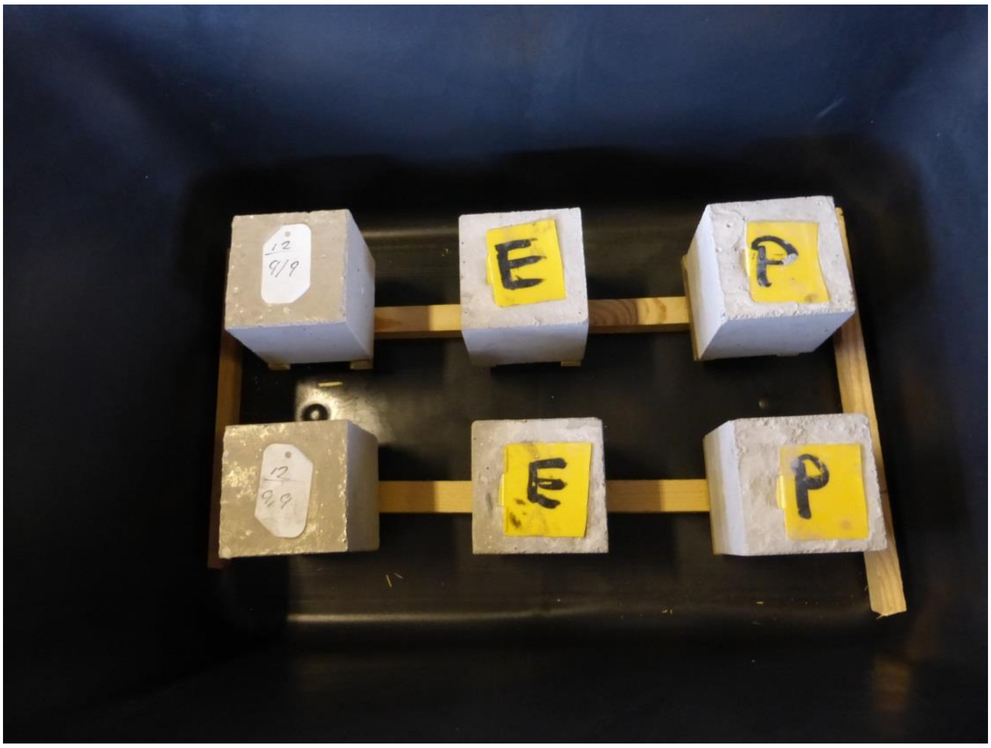

Figure 1. Concrete samples, Sweden. Left: Long lasting concrete; P, concrete in basic platform; E, concrete in wall elements. The samples are placed on a wooden frame made of 20 mm x 20 mm strips at the bottom of a plastic container. During exposure the labels were on the bottom. Samples were placed randomly in each box.

Figure 2. Room with constant temperature 20 °C for exposure of concrete samples to acidified and non-acidified cattle slurry. In the figure the container with acidified slurry and concrete samples is placed in the room and fitted with a non-airtight cover.

Routines during exposure

The following routine checks and measurements were performed during the exposure of the concrete samples:

- The slurry and air temperatures were recorded continuously with temperature loggers (PC-logger AAC-2f, Intab Interface-Teknik AB, Stenkullen, Sweden), data being recorded every third hour.
- Crust formation on the slurry surface was checked regularly.
- The slurry pH was measured in both treatments following gentle manual stirring (Figure 3). Acid was added, if necessary, to maintain pH<5.5. The pH was measured with an electrode pH meter Hanna Instruments Edge blue Serie No. C0211905E with a sensor in a plastic cover (Electrode pH-HALO Bluetooth(R) Plastic (Serie No. C4AD79). The slurry temperature was also measured with the instrument.
- To prevent insulating barriers developing on concrete sample surfaces, the samples were checked for crust formation, with the instruction to scrape away the crust.

- The level of slurry in the containers was checked regularly. After one year, the concrete samples were put into new batches of fresh slurry to imitate practice on farms. If the slurry levels were too low between fillings, slurry was also added to get a sufficiently thick (about 30 mm) layer above the concrete samples.

Figure 3. Measuring pH in container with acidified slurry to follow buffering before starting exposure of concrete samples at pH<5.5.

Finalisation of experiment

After nearly two years exposure, the experiment was finalised in November 2018 as follows:

1. The slurry level and crust formation on the slurry surface were measured.
2. The slurry was gently manually stirred in both treatments and its pH was measured. Loggers for slurry and air temperature, respectively, were collected, marked and taken to the office for downloading the data.
3. Concrete samples were taken out one by one, washed gently with water and put into labelled plastic bags marked as below.

ID	Slurry	Concrete quality
A1 (P)*	A) Cattle slurry, no acid	1) w/c m 0.59, (quality of ground plate of liquid storage)
A2 (E)	A) Cattle slurry, no acid	2) w/c m 0.48, (quality of wall element of storage)
A3 (12, 9/9)	A) Cattle slurry, no acid	3) Long lasting quality (LLC)
B1 (P)	B) Cattle slurry, acid, pH<5.5	1) w/c m 0.59, (quality of ground plate of liquid storage)
B2 (E)	B) Cattle slurry, acid, pH<5.5	2) w/c m 0.48, (quality of wall element of storage)
B3 (12, 9/9)	B) Cattle slurry, acid, pH<5.5	3) Long lasting quality (LLC)

*ID in brackets originated from manufacturer ABetong

4. The samples were delivered to RISE CBI's concrete laboratory where the structural analyses were performed.

Structural analysis of concrete samples

Structural analysis was performed using petrographic microscopy techniques to examine the effects of exposure to two potentially aggressive environments, non-acidified and acidified cattle slurry, on concrete with three different mixes.

Polished thin sections were made from concrete samples labelled A1 ("P, non-acidified cattle slurry"), A2 ("E, non-acidified cattle slurry"), A3 ("12 9/9, non-acidified cattle slurry"), B1 ("P, acidified cattle slurry"), B2 ("E, acidified cattle slurry"), B3 ("12 9/9, acidified cattle slurry").

The studied surfaces in the concrete samples were oriented vertically in the plastic containers. The samples were cut perpendicularly to the studied surfaces, at approximately half-height of the sample cube. The size of the polished sections and thin sections was approximately 50x25 mm.

The polished sections were evaluated with a stereo microscope (magnification up to 65 times). The thin sections of concrete, thickness 0.025 mm, were prepared from concrete impregnated with epoxy mixed with a fluorescent dye. The thin sections were evaluated using a polarising microscope (magnification up to 1000 times) and sources for visible and UV light.

Results and discussions

Storage conditions (air temperature, filling and reacidification)

Figure 4 shows the pH in the two slurry containers, with and without acid added, during the first year of exposure. A similar pattern was seen in the second year of exposure. After the pH had been checked, acid was added if it exceeded about pH 6. For the first exposure period, the total amount of acid added corresponded to 7.8 litres of concentrated acid per m^3.

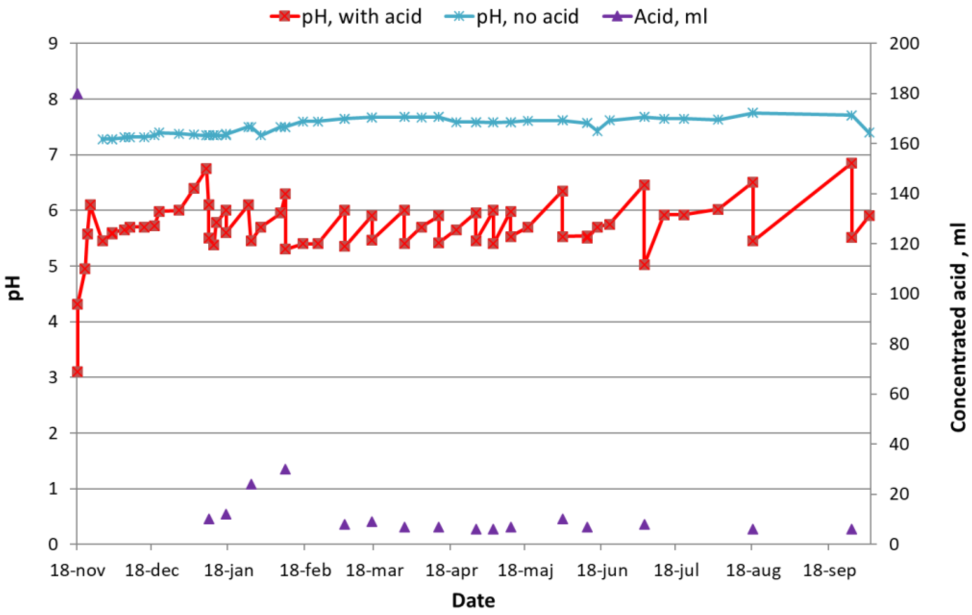

Figure 4. The cattle slurry pH during exposure of concrete samples in slurry with and without acid addition, first period 18 November 2016 to 4 October 2017. Concrete samples were placed into the slurry 2 December 2016.

Slurry properties

In Table 2, the properties of CS and DCS are presented at start and end of the two exposure periods: period 1 from 2 December 2016 - 4 October 2017; period 2 from 4 October 2017 – 6 November 2018.

The concentrations could be expected to be raised a bit due to some small addition of slurry during storage because of evaporation. However, this is not the case for nitrogen, as it could be volatilised as ammonia. For slurry without acid, most of the NH_4-N had disappeared during storage, while the NH_4-N concentrations for acidified slurry were about the same or higher at end as at start. The repeated addition of acid during storage gave higher concentrations of S in the end compared to start for the acidified slurry. The analysis was made on samples that had been frozen. For measuring of pH, it is recommended to measure of fresh samples. Perhaps this is an explanation for the high pH of acidified CS at Start 2, or it could be a laboratory error. The fresh measurements showed pH 5.5, and it was maintained in the same way as during the first year of exposure.

Table 2. Properties of cattle slurry (CS) and digested cattle slurry (DCS), without and with acid at the start and end of storage, first and second years. The analyses were performed on previously frozen samples. The pH in fresh slurry, first year, see Figure 4

				kg per tonne (wet basis)								
Slurry type	Time	TS, %	VS, % of TS	Tot-N	Org-N	NH_4-N	P	K	S	Tot-C	pH	Tot-C /Tot-N
CS, no acid	Start 1	6.7	82.8	3.3	1.6	1.7	0.5	2.9	0.3	30.8	7.4	9.4
	End 1	5.9	71.3	1.7	1.6	0.1	0.6	1.7	0.5	24.2	7.6	14.1
CS, with acid	Start 1	8.3	82.4	4.6	2.3	2.3	0.5	2.8	2.1	36.3	5.7	7.8
	End 1	8.7	75.0	5.0	3.0	2.0	0.5	3.7	5.0	31.3	6.7	6.3
CS, no acid	Start 2	7.2	81.8	2.9	1.7	1.2	0.4	2.5	0.4	33.1	7.2	11.4
	End 2	5.3	70.6	1.6	1.4	0.2	0.5	3.4	0.4	21.4	7.5	13.6
CS, with acid	Start 2	7.4	78.1	3.1	1.8	1.3	0.4	2.8	1.8	31.7	6.8	10.3
	End 2	8.1	74.7	4.8	2.9	1.9	0.4	3.6	4.7	29.4	6.6	6.1

The mean temperature in slurry during the two years was 19.9 °C.

Structural analysis of concrete samples

Polished sections in stereo microscope

Figures 5-10 show polished sections of concrete samples. The surfaces of the concrete cubes are in the upper and left part of the images. A millimetre scale is shown in the lower part of the figures.

The outer layer of the cement paste in samples exposed to acidified slurry (B-treatments) shows dark discoloration (see Figures 6, 8 and 10). The discoloration is visible on the polished sections in the outer 2-10 mm of the concrete from samples of all concrete qualities (B1, B2 and B3). The maximal depth of this discoloration (10 mm) was found in sample B1. Note that the binder in the “LLC” concrete in samples A3 and B3 is generally darker than in the “regular” concrete mixes in the other samples. We assume that the inner core of a sample cube represents the colour the concrete had prior to exposure to slurry.
No signs of cracking were observed on the polished concrete surfaces.

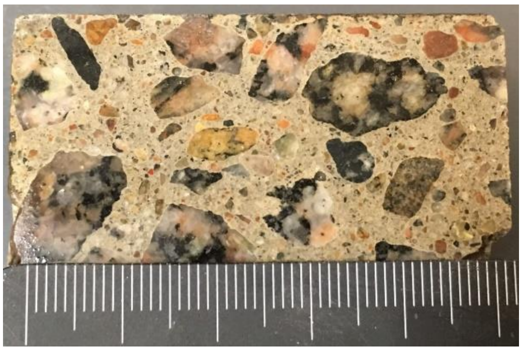

Figure 5. Sample A1 (No acid).

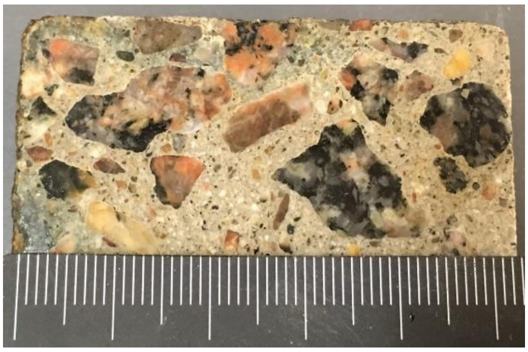

Figure 6. Sample B1 (Acid).

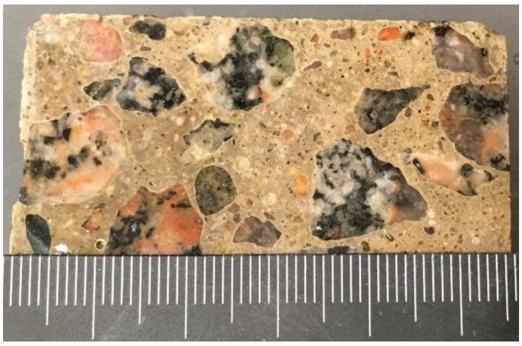

Figure 7. Sample A2 (No acid).

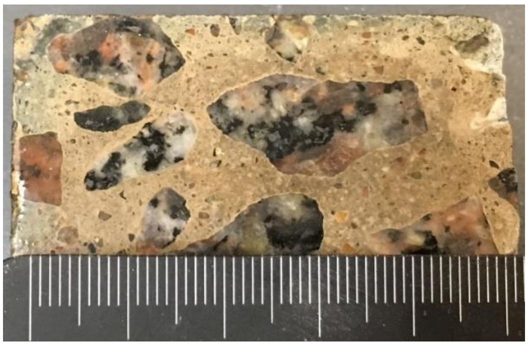

Figure 8. Sample B2 (Acid).

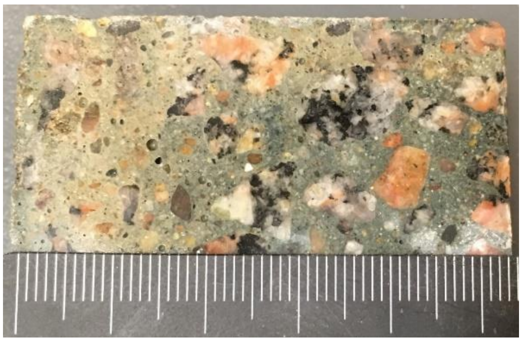

Figure 9. Sample A3 (No acid).

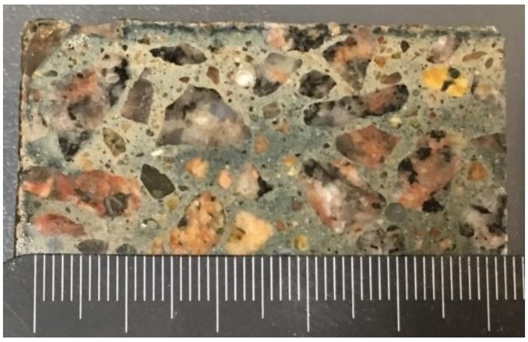

Figure 10. Sample B3 (Acid).

Thin sections in polarising microscope

Examples of concrete structures observed in the thin sections are shown in Figures 10-15. The images are taken in thin sections, using a polarising microscope. The width of the area in every image is 6.7 mm. All images show a depth interval in concrete of 0-5 mm, except for the image to the right in Figure 12 where the interval is 5-10 mm. The surfaces of the concrete samples are in the upper part of the images.

The outer layers of the concrete from samples A1, B1, A2, B2 and B3 show signs of weak chemical attack, characterised by an increase in capillary porosity in the cement paste (Figures 11-14 and 16). No porosity increase was observed in the sample A3 (“12 9/9, non-acidified cattle slurry”) (Figure 15).

There is a distinct difference in the maximum depth of the areas with increased capillary porosity between sample series A and B, where the larger depths are observed in concrete exposed to acidified slurry. We relate the increase in capillary porosity mainly to the decomposition and leaching of part of the calcium hydroxide in the cement paste due to moisture transport through the outer layers of the concrete. The leaching appears to be more effective the lower the pH in the environment the concrete is exposed to, which is to be expected.

Strong chemical attack, which can be defined as a breakdown of the structure of the concrete’s binder due to decomposition of the calcium-silicate hydrate and/or considerable micro-cracking of the concrete, was not observed in any of the analysed samples. Short micro-cracks up to 0.02 mm wide were observed in the thin sections of samples A2 and B2. However, the morphology and distribution of the cracks indicates that they are caused by drying shrinkage of the concrete and not by external chemical attack on the cement paste.

Secondary compounds in the air voids formed due to reactions related to chemical attack were not found in the thin sections.

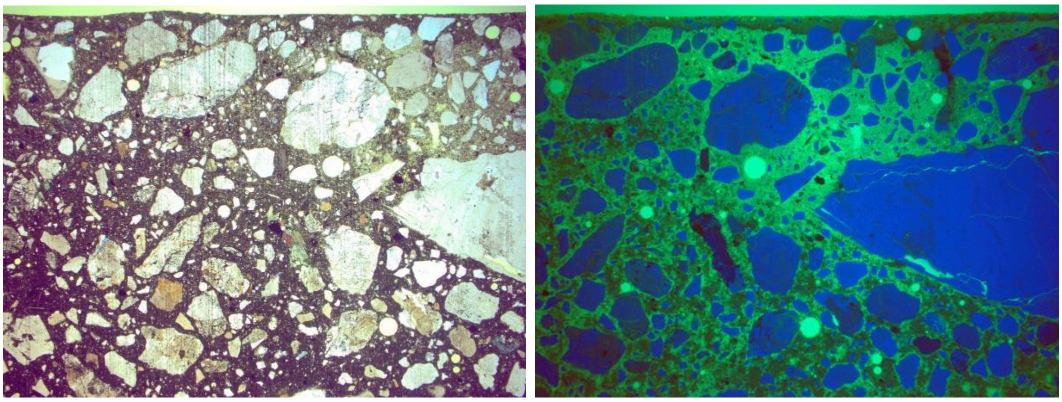

Figure 11. Sample A1, images taken in polarised light (left) and UV light (right).

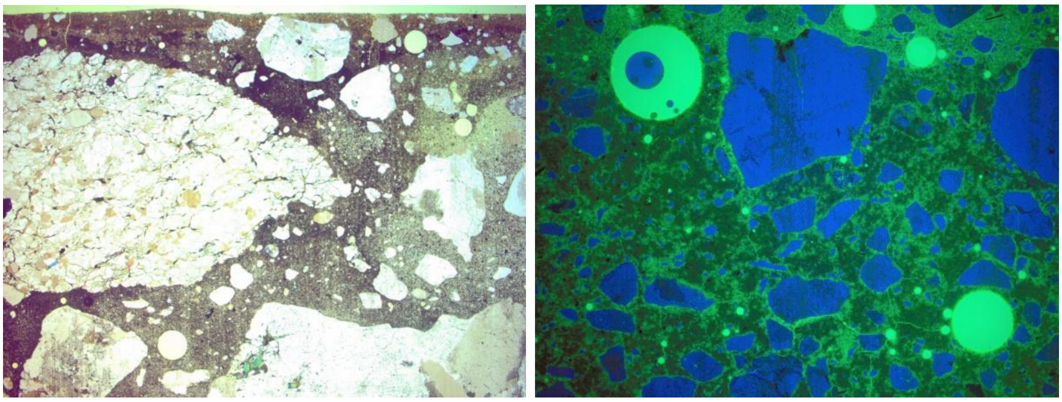

Figure 12. Sample B1, images taken in polarised light (left) and UV light (right).

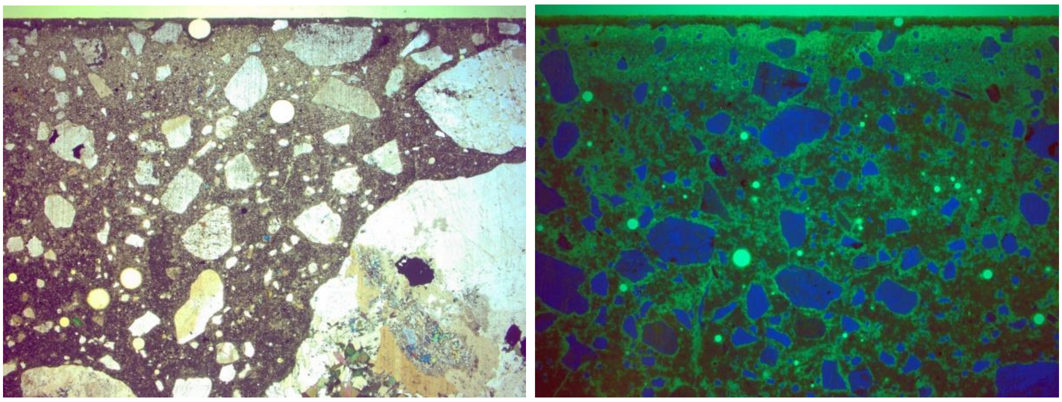

Figure 13. Sample A2, images taken in polarised light (left) and UV light (right).

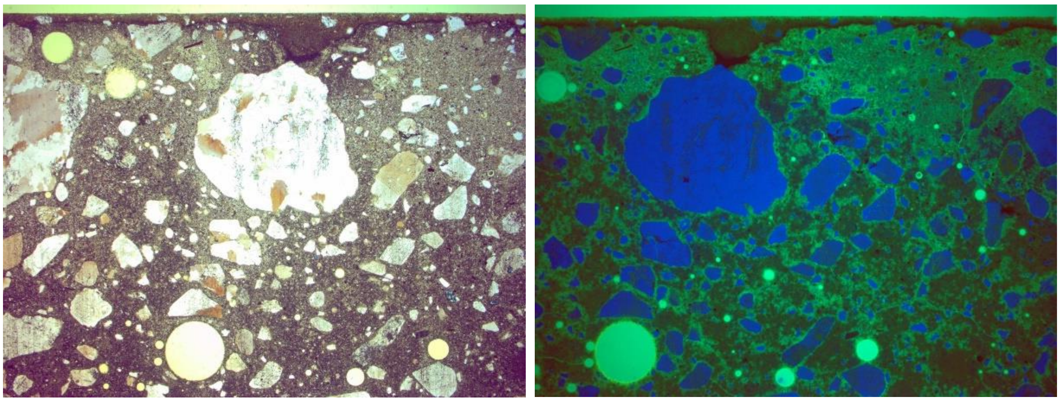

Figure 14. Sample B2, images taken in polarised light (left) and UV light (right).

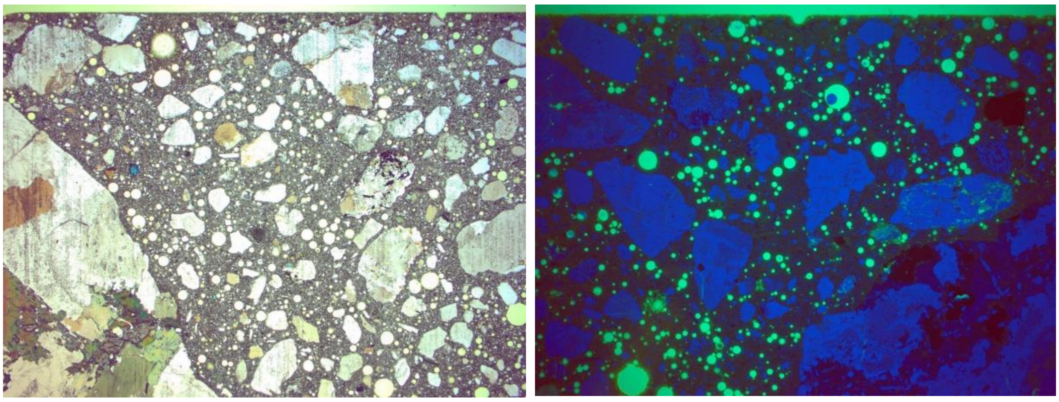

Figure 15. Sample A3, images taken in polarised light (left) and UV light (right).

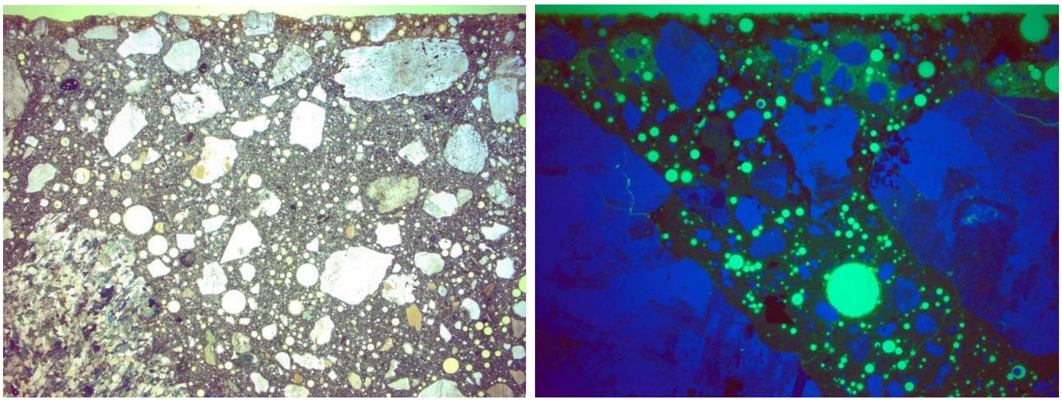

Figure 16. Sample B3, images taken in polarised light (left) and UV light (right).

Observations made in the petrographic analysis of the concrete samples are summarised in Tables 3-5. The samples consist of concrete with three qualities: “regular” concrete with w/c 0.59 (samples A1 and B1), “regular” concrete with w/c 0.48 (samples A2 and B2) and special “LCC” concrete mix designed for long durability in low-pH environments (samples A3 and B3).

Table 3. Evaluation of thin sections of concrete samples A1 ("P, non-acidified cattle slurry") and B1 ("P, acidified cattle slurry")

Sample	**A1**	**B1**
Depth of carbonatisation of the cement paste	0.2-2.5 mm	0.2-2.5 mm
Depth of increase in the capillary porosity (leaching of the cement paste)	2.5 mm	2.0-6.5 mm
Micro-cracks possibly caused by chemical attack	Not observed	Not observed
Depth of discoloration of the cement paste	Not observed	0.3 mm, brown
Decomposition of the calcium silicate hydrate	Not observed	Not observed
Precipitation of secondary compounds in the air voids	Not observed	Not observed

Table 4. Evaluation of thin sections of concrete samples A2 ("E, non-acidified cattle slurry") and B2 ("E, acidified cattle slurry")

Sample	**A2**	**B2**
Depth of carbonatisation of the cement paste	0.1-1.5 mm (1.5 mm around drying shrinkage micro-cracks)	Mostly 0.1-1 mm, 2.5 mm in one area around a micro-crack
Depth of increase in the capillary porosity (leaching of the cement paste)	1-1.5 mm	1-3.5 mm
Micro-cracks caused by chemical attack	A few short micro-cracks at depth 0-1 mm, max. width 0.02 mm	A few short micro-cracks at depth 0-2 mm, max. width 0.01 mm
Depth of discoloration of the cement paste	Not observed	0.3 mm, brown
Decomposition of the calcium silicate hydrate	Not observed	Not observed
Precipitation of secondary compounds in the air voids	Not observed	Not observed

Table 5. Evaluation of thin sections of concrete samples A3 ("12 9/9, non-acidified cattle slurry") and B3 ("12 9/9, acidified cattle slurry")

Sample	**A3**	**B3**
Depth of carbonatisation of the cement paste	Mostly approx. 0.1 mm, 2.0 mm in small areas	0.3-1.0 mm
Depth of increase in the capillary porosity (leaching of the cement paste)	Not observed	0-1 mm
Micro-cracks caused by chemical attack	Not observed	Not observed
Depth of discoloration of the cement paste	Not observed	0.3 mm, brown
Decomposition of the calcium silicate hydrate	Not observed	Not observed
Precipitation of secondary compounds in the air voids	Not observed	Not observed

The results show that acidified slurry is more chemically aggressive to the cement paste in all the concrete mixes analysed. The extent of the chemical attack correlates with the initial quality of the concrete mix (water-powder ratio and type of binder). The LLC concrete shows better resistance to chemical attack. The maximum depths of the weak chemical attack in the samples A3 and B3 are 0 mm (no signs of deterioration) and 1 mm respectively.

As the exposure time was rather short (two years), and only an area 25 mm wide was studied in every concrete sample, it is in our opinion not possible to draw any detailed conclusions about the differences in the degree of chemical attack associated with acidified slurry compared with regular slurry. However, there is clear indication of an increase in leaching potential for slurry with added acid.

Conclusions

The results of the study show that the acidified slurry is more chemically aggressive to the cement paste in all the concrete mixes analysed. This may be explained by the solution's lower pH.

The extent of the chemical attack correlates to the initial quality of the concrete mix (water-powder ratio and type of binder). The deepest chemical attack was observed in samples A1 and B1 consisting of "regular" concrete mix with w/c 0.59. The "long lasting quality" (LLC) concrete with a binder specially developed for low-pH environments shows markedly better resistance to chemical attack.

The effects of the chemical attack on concrete after two years of exposure can be classified as weak, consisting mainly of an increase in the capillary porosity of the cement paste in the outer layer of the concrete. The increase in porosity is thought to be due to the partial leaching of calcium hydroxide.

Baltic Slurry Acidification

www.balticslurry.eu

Summary of the project

Baltic Slurry Acidification is an agro-environmental project financed by Interreg Baltic Sea Region under the priority area Natural resources and specific objective Clear Waters. The aim of the project is to reduce nitrogen losses from livestock production by promoting the use of slurry acidification techniques in the Baltic Sea Region and thus to mitigate eutrophication of the Baltic Sea. Baltic Slurry Acidification project started on March 2016 and was finished in February 2019.

Summary of the report

Samples of three different concrete qualities were prepared and hardened, before exposure to cattle slurry without sulphuric acid and with sulphuric acid added until pH<5.5. The samples were exposed for two years. The results of the study show that the acidified slurry is more chemically aggressive to the cement paste in all the concrete mixes analysed. The extent of the chemical attack correlates with the initial quality of the concrete mix.

Contributing partner

Research Institutes of Sweden