



Aalborg University  
*Department of the Built Environment*  
Master's thesis in Water and Environmental Engineering

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Corrosion resistance of an experimental highly alkaline  
shotcrete to biogenic sulfuric acid in a controlled sewer  
environment

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## Abstract

The effect of biogenic sulfuric acid corrosion is evaluated on an experimental highly alkaline shotcrete (ASC). The idea is to use the shotcrete as a measure to reduce the corrosion not only in the new sewer mains, but also in the ones already affected by heavy corrosion. The study evaluates mainly two processes, carbonation and acid corrosion and in order to evaluate the relevancy of the results, the study is conducted also on a standard type of concrete (STDC) commonly found in Danish sewers. In a reactor, the carbon dioxide uptake rate is measured and it is found that the uptake is approximately 24 times higher in the ASC than in STDC. The carbonation depth is then estimated with a simple model and a 10-12 mm layer of ASC is fully carbonated in 2-3 months. Samples of both concretes are then placed in an incubator with sewer-like conditions for 2 months in order to enhance the growth of sulfur oxidizing bacteria. Each sample is then placed in a smaller reactor and the uptake of hydrogen sulfide ( $\text{H}_2\text{S}$ ) is measured. Subsequently, the surface specific  $\text{H}_2\text{S}$  uptake rate is calculated and simulated with  $n^{\text{th}}$  order kinetics. The uptake rate for STDC is found in line with other studies on the same concrete, while for ASC the uptake at concentrations of  $\text{H}_2\text{S}$  below 40 ppm is twice as high. Based on these results, the corrosion rates at different  $\text{H}_2\text{S}$  concentrations are calculated. It is found that both STDC and ASC have similar corrosion rates at constant concentrations below 100 ppm, resulting in a 10 mm layer being corroded in approximately 3.8 years for STDC and 4.3 for ASC at 100 ppm of  $\text{H}_2\text{S}$ . The yearly corrosion rates are then re-calculated based on a 365 days time series of  $\text{H}_2\text{S}$  measurements at a manhole downstream of a force main close to the wastewater treatment plant of Ikast, where heavy corrosion has been reported. It is found that the corrosion rate is approximately  $0.91 \text{ mm yr}^{-1}$  with a 10 mm layer expected to be fully corroded in almost 11 years. Although it is found that ASC behaves similarly to STDC in terms of corrosion rates, the fact that the uptake rate of  $\text{H}_2\text{S}$  is greatly higher in ASC results in lower concentrations of  $\text{H}_2\text{S}$  in the downstream sections thereby preserving the concrete further down the sewer network. Combining this result with the fact that ASC can be easily replaced with the help of a concrete spraying machine, it is believed that ASC poses as a valid tool for preserving the concrete in sewer mains reducing the cost of overall maintenance.



## Reading guide

This report is a result of the thesis module of the 10<sup>th</sup> semester of Water and Environmental Engineering at Aalborg University. The report has been written in the period from February 3<sup>rd</sup> 2020 to June 10, 2020.

The thesis consists of a main report with an appendix. Appendix A and B are found in the report while appendix C is found as an electronic appendix attached to the report. A short description is given for each electronic appendix.

References will be in brackets with author followed up by year of publication, for example (Saetta et al., 1993). The references are either placed within or after the section where they are applied. When referring to a web-page either the author or the name of the web-page is specified, for example (King, 2007).

The references in the bibliography are written in alphabetical order. Equations, tables and figures are numbered according to the chapter or appendix with number or letter and the order of presenting them, for example equation 5.5 is the fifth equation in chapter 5. Figures without a reference in the caption are made by the author and by Assoc. Prof. Asbjørn H. Nielsen.



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In recent years there has been an increase in damages and failures in the sewers caused by the corrosion generated from oxidation of hydrogen sulfide ( $H_2S$ ). The issue is of particular interest as failures in the sewer network can result in disastrous accidents such as sewer and even street collapses. These events have social, health and economical impacts and the latter can be quite extensive. As an example, in 1991 it was estimated that the cost of repair or replacement of every kilometer of the sewer in Los Angeles was 3.2 mln \$ (USEPA, 1991) and in 2006, Nakhla et al. determined that the cost of repair of the entire German sewer network as a result of hydrogen sulfide induced corrosion was around 40 bln \$.

The issue of corrosion in the sewers was known and documented in late 19<sup>th</sup> century as reported by Olmstead and Hamlin (1900) in Los Angeles where in some sections of the network about a quarter of the wall's thickness had been destroyed in just 5 years of service. At the time, the specific cause of these events was not known and it was only inferred that they were connected with some sort of sewer gases. It was only in the 1940's, as a result of research in both USA and Australia (Wells et al., 2009), that the corrosion affecting concrete and metal structures in the sewers was found to be a result of bacterial production of sulfuric acid via oxidization of  $H_2S$ . The 1950's saw the beginning of lined pipes as a concrete protection alternative (USEPA, 1991), but it was not until the 1960's that municipalities around the world recognized the problem and started taking active measures (Hvitved-Jacobsen et al., 2013; USEPA, 1991). Later on, in the 1980's a spike in the rates of corrosion was recorded in USA and Europe, probably in relation to the decrease in the concentration of toxic components in the sewers as a result of governments policies and also due to the increasing temperature of the wastewater (Tator, 2003; Gu et al., 1998). Today the process is well understood and there is a large number of interventions aimed at ensuring greater protection of sewer structures from corrosion. All of them are effective in a different way, but none of them represent a definitive solution to the problem and must therefore be used in combination with each other depending on each specific case.

This topic is particularly relevant in Denmark, where in recent years the wastewater treatment has been centralized to few major treatment plants and the drinking water consumption has decreased by 38% over the last 31 years (DANVA, 2019). Consequently, the residence time of wastewater in the sewers has increased and a number of pressure mains have been built. These two factors, and other minor ones, have contributed heavily in the increase of  $H_2S$  production and release in the sewer atmosphere. Thus, there has been an increase in the corrosion rates of concrete and metal structures in the sewers and this has attracted the attention of several municipalities which are taking measures to handle the problem. In particular, the municipality of Ikast-Brande is trying to manage the problem by using

an experimental coating shotcrete that should neutralize sulfuric acid and therefore protect the structural concrete underneath. The spraying of the concrete is also part of an experimental technology which aims at developing a machine for the coating of sewer mains. At the time of the report, both technologies are being tested on a large sewer pipe where heavy corrosion has been reported. The coating concrete is provided by Marlon Tørmørtel A/S and the spraying machine by Villy Poulsen A/S. This reports intends to understand and estimate the lifetime of such concrete in an ideal sewer environment where the conditions are favourable for the formation of sulfuric acid on the concrete surface and the concrete's capability in reducing the concentration of hydrogen sulfide.

## 1.1 Technology and implementation

The combination of the experimental alkaline shotcrete and the spraying machine aims at the same goal of reducing the microbial induced corrosion in standard sewers concrete and reduce the cost of maintenance. There are numerous tools that can be implemented in a sewer system in order to slow down the corrosion process which address the issue from different angles. This technology focuses on the decrease of hydrogen sulfide in the gas phase and the neutralization of the acid on the concrete surface. At the time of the report and as far as the knowledge of the author goes, there is no technology that can achieve this goal in an efficient and economically advantageous way. As mentioned before, this is a two steps process, the concrete mix is first prepared and then sprayed on the inner walls of a sewer main using a specific machine. Then follows an activation time in which the concrete begins to oxidize  $H_2S$  resulting in the formation of sulfuric acid ( $H_2SO_4$ ) which is neutralized by the concrete's alkalinity. Figure 1.1 shows the spraying machine at a test site.



**Figure 1.1:** Concrete spraying machine at a test site with freshly sprayed concrete.

In August 2019 the coating concrete has been applied in a 62 m long pipe outside the wastewater treatment plant of Ikast, in the Mid Jutland region of Denmark. The reason for this is the heavy corrosion reported in the concrete mains downstream of a pressure main. Therefore, a section has been coated with the intent to both reduce the rate of corrosion and the concentration of  $H_2S$ .

## 1.2 Strategy of the study

In order to understand the quality and the effectiveness of the experimental shotcrete, the related chemical and biological processes which lead to corrosion are analysed. A comparison is made with standard sewer concrete and for this matter samples of commonly used concrete in Danish sewers are used. Firstly, the chemical process of carbonation is evaluated followed by an analyses of the biological oxidation of  $\text{H}_2\text{S}$ . Secondly, the data gathered is combined with other concrete parameters and alkalinity measurements which, using a mathematical model, lead to the estimate of the corrosion rates at different  $\text{H}_2\text{S}$  concentrations.

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## 2.1 Introduction

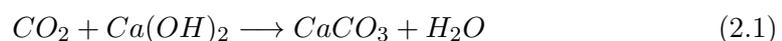
Concrete is widely used in the world of engineering due to its structural capacity and the relatively low cost of manufacturing. In structural engineering the degradation of concrete is crucial particularly in reinforced concrete, where the corrosion exposes the inside steel rebar to phenomena like cracking and spalling resulting in an overall decrease in the structural load carrying capacity. In the sewers environment, the loss of concrete due to microbial induced corrosion (MIC) begins when the pH falls below a certain value. In both cases the first step of degradation is the process known as carbonation.

Carbonation is a chemical process in which carbon dioxide ( $\text{CO}_2$ ) diffuses into the liquid phase in the pores of concrete reacting with the calcium in the calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) and with calcium silicate hydrate (C-S-H). This results in the formation of calcium carbonate ( $\text{CaCO}_3$ ). The process happens in the pores of concrete and begins immediately when fresh concrete is exposed to air, in a matter of days or even hours. The main consequence of such process is the lowering of the pH in the pores creating a favourable environment for bacteria growth. A fresh concrete has a pH of about 12.5 and during carbonation it drops to approximately 8.5, which leads the beginning of MIC. (Saetta et al., 1993; Jung et al., 2011)

Other major consequences of carbonation are the changes in pore volume and the corrosion of the steel bars in the case of reinforced concrete. The first causes micro fractures, leading to an increase in the permeability of the concrete, hence increasing the carbonation process (Saetta et al., 1993) and the second results in a decrease in mechanical strength, decreasing the durability and therefore the safety of the structure.

## 2.2 Process in details

Carbon dioxide in the atmosphere diffuses into the liquid phase in the pores of the concrete. It then binds with water to form carbonic acid ( $\text{H}_2\text{CO}_3$ ) which reacts with other chemical compounds and elements to form carbonates. One of the predominant compounds in concrete is calcium hydroxide which reacts with the carbonic acid releasing water and calcium carbonate and this is then the dominant reaction, which is shown below in a simple formulation.



This reaction requires water as a vector, thus if the concrete is completely dry the reaction cannot happen. The same goes for the case when the pores in concrete are

completely filled with water, as  $\text{CO}_2$  dissolves slowly in water. Therefore, in order for the process to develop, the pores must be partially filled with water, which is also the condition appearing most often in concrete. (Saetta et al., 1993) There are other important factors in the process which are listed and explained below.

### 2.2.1 Humidity

As mentioned before, humidity plays a crucial role in the rate of carbonation. Carbon dioxide found in the atmosphere forms an acidic solution with water which then reacts with the hydrated concrete resulting in a decrease in pH. Therefore, when the pores in the concrete are completely filled with water the diffusion of carbon dioxide is much slower, because the rate of diffusion in water can be up to 40 times slower than air. There must then be a balance between air and water in order for the reaction to happen at a fast pace and Bertolini et al. (2014) suggests a relative humidity (RH) of 60%-80% in order for the process to be fastest. Generally, the sewer environment has high levels of RH, in ranges between 85% up to 100% (Sanders et al., 1989; Joseph et al., 2012).

### 2.2.2 $\text{CO}_2$ concentration

The concentration of  $\text{CO}_2$  is another crucial parameter in the rate of the process. The more  $\text{CO}_2$  is in the atmosphere and the faster the reaction will be. Usually the amount of  $\text{CO}_2$  in the sewer can vary between 300 ppm and 1000 ppm (Bertolini et al., 2014) while other sources, like Hvitved-Jacobsen et al. (2013) suggest values always above 500 ppm, indicating biological activity in the wastewater, and at max 10000 ppm.

### 2.2.3 Temperature

The higher the temperature and the faster the reaction will be due to an increase in the solubility of compounds like  $\text{O}_2$  and an increase in the kinetic energy of the molecules which will penetrate deeper and faster in the concrete (Tuutti, 1982). A study by Liu et al. (2019) shows a direct correlation between temperature rise and increased carbonation depth in a range of temperatures between 10 °C and 30 °C.

### 2.2.4 Concrete composition

In the making of the concrete mixture a certain water to cement ratio (w/c) is adopted. A low w/c results in smaller pores and as a consequence it is harder for the  $\text{CO}_2$  to penetrate. Therefore a low w/c results in a slower rate of carbonation. Moreover, it is not uncommon to find cracks and micro fractures in concrete as a result of volume changes between the cement paste and the aggregates. Whether caused by temperature excursion, particular loads or other factors, what is crucial is the increase in permeability resulting in a faster and deeper carbonation front. (Tuutti, 1982)

## 2.3 Process rate and depth

It is generally estimated that the rate of the reaction is proportional to the square root of time. For example, a carbonated depth of 3 mm takes an approximate time of 9 years. (Tuutti, 1982; Torres et al., 2017) Among all the factors listed above, perhaps the one that limits the rate of carbonation the most is the porosity. While humidity, temperature and CO<sub>2</sub> can generally be found in similar ranges of values among the different sewer environments, porosity poses a physical obstacle. In order for the carbonation front to penetrate deeper, factors such as CO<sub>2</sub> and humidity must also be able to advance in the layer. Thus, when the porosity is high the pores are more connected to one another and the process advances rapidly and vice versa.

There is a close correlation between carbonation and the production of sulfuric acid which results in the corrosion of concrete in the sewers. As a result of the lowering of the pH and under certain conditions of humidity, CO<sub>2</sub> and atmospheric oxygen, bacteria which oxidize hydrogen sulfide grow on the outer layer of the concrete above the waterline of the wastewater. (Apgar et al., 2007) Therefore, the next chapter will present the topic of hydrogen sulfide induced corrosion.



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### 3.1 Introduction

Hydrogen sulfide is a colorless, highly malodorous gas and is responsible for 99% of the corrosion of concrete in the sewers (Apgar et al., 2007). In recent years the amount of this gas has increased and consequently concrete corrosion has increased as well. In order to understand the problem an introduction to the life cycle of sulfide is presented.

### 3.2 Sources of sulfide in the sewers

Concerning domestic discharges, sources of sulfur are found in detergents, excreta as well as albuminoid proteins present in milk and eggs. Usually in domestic wastewater the concentration of organic sulfur is 1-3 mg/L. The major sources however can be industries such as breweries, slaughterhouses, chemical plants, oil refineries and paper making. More in general, the sulfur in wastewater is usually in the form of sulfates which are universally found in drinking water, specially when the water is abstracted from underground reservoirs (as per most of Denmark)(Apgar et al., 2007; Geddes, 2014). Nonetheless, Bowker et al. (1992) reports that concentrations as low as 0.1 mg/L are still enough to produce substantial H<sub>2</sub>S concentrations in the sewer atmosphere.

Two types of sulphate compounds can be found in the wastewater, organic and inorganic and the latter is the most concerning as it is the main source of sulfate ions (SO<sub>4</sub><sup>-</sup>). Specific bacteria reduce SO<sub>4</sub><sup>-</sup> releasing sulfide. (Sanders et al., 1989) Sulfide is usually absent in domestic wastewater and it is generated via a biological process that take place under the waterline of the wastewater. In particular, a biological slime layer forms below the water level and it is made of bacteria. The slime layer is made of three sub-layers which interact with each other: aerobic, anaerobic and inert. They are shown in figure 3.1 and the interactions are briefly described in the three following subsections.

#### 3.2.1 Aerobic slime layer

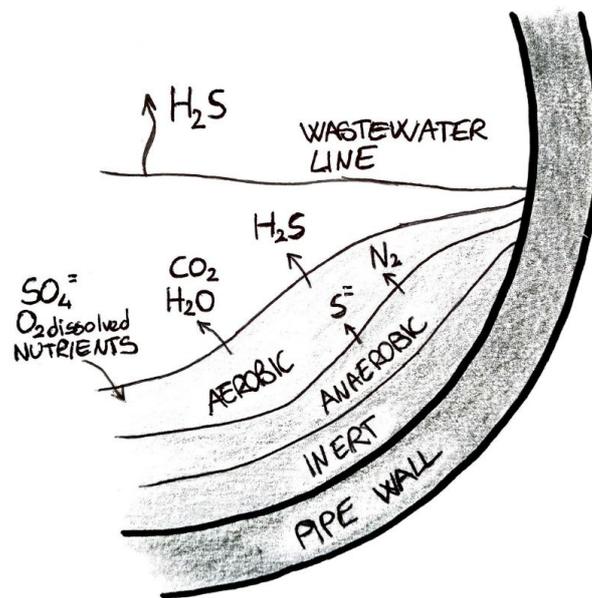
This layer is present when there is enough oxygen dissolved in the wastewater which is needed by the bacteria to carry their life processes. Among the different processes, the bacteria oxidize sulfide (S<sup>=</sup>) coming from the underneath layer to sulfate and release other harmless compounds. Byproducts of the anaerobic decomposition include water and carbon dioxide.

### 3.2.2 Anaerobic slime layer

In this layer the bacteria use combined oxygen from nitrate ( $\text{NO}_3^-$ ), nitrite ( $\text{NO}_2^-$ ), sulfite ( $\text{SO}_3^-$ ) and sulfate. As a consequence, nitrogen gas ( $\text{N}_2$ ) is released together with sulfide and consequently hydrogen sulfide. However, since nitrate and nitrite are not often present in wastewater, the release of hydrogen sulfide will be predominant corresponding to the release of nitrogen gas. Sulfide is released and diffuses in the aerobic layer and if enough oxygen is present, sulfide can be oxidized back to sulfate.

### 3.2.3 Inert slime layer

The inert layer, contrary to its name, is not really inert. This layer interacts closely with the anaerobic layer in the matter that  $\text{BOD}_5$  is converted anaerobically generating fermentation products. Such products are then used by the bacteria in the aerobic layer in order to convert sulfate to sulfide.



**Figure 3.1:** Schematics of the slime layer interactions in a sewer environment.

There are several factors that enhance the production and the release of hydrogen sulfide and some of the most relevant are listed below:

- High  $\text{BOD}_5$  concentration
- High wastewater temperature
- Long sewer network
- Forced mains and pumping stations
- Low dissolved oxygen in the wastewater
- High turbulence in the wastewater

(Apgar et al., 2007)

Turbulence, however, can also be beneficial. If the amount of dissolved  $H_2S$  in the liquid phase is very low, turbulence can promote the diffusion of oxygen in the wastewater thereby reducing the release of  $H_2S$ . However, Bowker et al. (1992) reports that if the wastewater has low amounts of  $H_2S$  (0.1 to 0.2 mg/L) the result is a substantial increase in the rate of release in the gas phase, promoting corrosion.

### 3.3 Sulfide induced concrete corrosion

On a simple level, once hydrogen sulfide is released into the sewer atmosphere it is taken up by specific bacteria which are present on the concrete surface above the wastewater line. As a result, these bacteria secrete sulfuric acid which corrodes and weakens the concrete. The danger of this scenario is the possibility of a structural failure and a collapse of the sewer.

#### 3.3.1 Bacterial growth and production of sulfuric acid

Sulfuric acid is produced by specific bacteria living on the concrete above the waterline. In order for these bacteria to colonize the sewers and to proliferate, certain conditions have to be met. When concrete is freshly made it has a pH around 12 and 13 and for this reason bacteria cannot grow because the high pH dissolves the protein in the cell wall. In time, however, the pH of concrete will fall and around a pH of 9 bacteria start growing on the surface. There are several types of bacteria that produce sulfuric acid and one more reason why they are a concern is that different types can live at different pH. In fact, the bacteria that produce sulfuric acid can be found in a range of pH from 9 down to 0.5. (Apgar et al., 2007)

#### 3.3.2 Concrete decomposition

As mentioned before, freshly cast concrete has a high pH and this is because of the high presence of calcium hydroxide in its volume. When sulfuric acid is produced by bacteria and comes in contact with calcium hydroxide and calcium carbonate, it results in the formation of calcium sulfate ( $CaSO_4$ ) more commonly known as gypsum according to the following expression:



Gypsum is a very common mineral which has a relatively low structural strength (2/10 on the Mohs hardness scale) (King, 2007). It is obvious then that the formation of gypsum decreases the structural strength of the concrete, especially when wet, increasing the danger of a collapse. (Apgar et al., 2007)

### 3.4 Corrosion rates

Corrosion rates are commonly expressed in mm per year of either lost concrete material or concrete with a significant reduction in mechanical strength. It is measured from the surface inward and common rates can be found at about 3 mm  $yr^{-1}$  while high rates are around 5 mm  $yr^{-1}$  with the exception of extreme cases where

### 3. BIOGENIC SULFURIC ACID CORROSION

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rates where observed at even  $25 \text{ mm yr}^{-1}$  (Sanders et al., 1989; Hvitved-Jacobsen et al., 2013).

Usually the formation of acid is higher near the water line due to a number of reasons: the high moisture content that can result from capillarity, the presence of residuals that can clog on the sides bringing more nutrients for the bacteria and more  $\text{CO}_2$ ,  $\text{H}_2\text{S}$  and ammoniacal nitrogen. This has been confirmed particularly in round sewers, where a high corrosion rate is also found in the crown area, probably due to the high moisture (Parcer, 1997; Bowker et al., 1992).

Interestingly, when the moisture on the concrete surface is high, the sulfuric acid produced can flow down from the side wall or drip from the crown in the wastewater and be neutralized without corroding any concrete. Some estimate that this amount of acid might be as much as 50% of the total acid produced (Sanders et al., 1989), but due to the lack of additional proof and in order to keep a conservative approach, the eventuality of sulfuric acid flowing in the wastewater is not taken into account.

## 4.1 Introduction

Three laboratory experiments are set up to evaluate carbonation and corrosion for both types of concrete. The first is a test on the CO<sub>2</sub> uptake rate followed by a test on the H<sub>2</sub>S uptake rate, which will lead to an estimation of the corrosion depth over time. All the experiments are conducted in a controlled environment. Initially an alkalinity test was planned for both concretes, but due to experimental limitations explained later in section 4.6, the results from other researches are used. Before any experiment, a short description of each sample is presented.

## 4.2 Concrete Samples

Two types of concrete are tested, a standard type which is commonly used in sewers in Denmark and an experimental shotcrete with a high degree of alkalinity. The known parameters prior to any test are shown in table 4.1 and a sample of each type of concrete is shown in figure 4.1. For practicality, the standard concrete is defined as STDC followed by a number indicating the specific sample, the alkaline shotcrete is abbreviated as ASC, again followed by a number indicating the specific sample. A total of 5 samples are tested and each sample has a different size.

**Table 4.1:** Specifications of the tested concrete samples prior to any test.\*Average among the samples of each type of concrete.

| Sample | Area [cm <sup>2</sup> ] | Volume [cm <sup>3</sup> ] | Weight [g] | Density* [kg m <sup>-3</sup> ] |
|--------|-------------------------|---------------------------|------------|--------------------------------|
| STDC1  | 153.7                   | 118.4                     | 267.4      |                                |
| STDC2  | 153.2                   | 114.5                     | 262.4      | 2318                           |
| STDC3  | 143.0                   | 96.7                      | 226.2      |                                |
| ASC1   | 119.8                   | 66.3                      | 123.4      | 1926                           |
| ASC2   | 145.9                   | 86.6                      | 172.5      |                                |

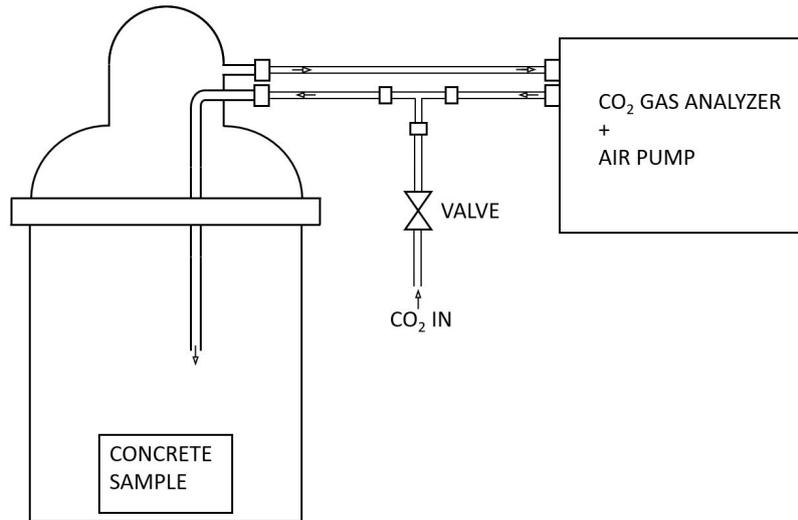


**Figure 4.1:** Sample ASC1 (left) and STDC1 (right). Both samples are presented after being ground in order to remove the carbonated layer and expose an unreacted surface.

### 4.3 Carbonation test

Different types of concrete behave in different ways when exposed to a sewer environment. The carbonation of concrete is one of the key processes in the development of the corrosion because it is the first step in the growth of bacteria that produce sulfuric acid. In order to have a better understanding of the response of the coating concrete to the acid, a carbonation test is conducted so to estimate the time that it would take for the bacteria to colonize the surface and how much is the depth of the carbonated layer corresponding to time.

The carbonation process is evaluated under a controlled environment, where the samples of concrete are placed in a sealed reactor, one at a time, and  $\text{CO}_2$  is injected at different intervals and with similar volumes. The sensor used is the Li-820  $\text{CO}_2$  Gas Analyzer by Li-Cor. The  $\text{CO}_2$  concentration is measured every 2 seconds with a maximum range of 10 000 ppm. The setup is shown in figure 4.2.



**Figure 4.2:** Carbonation test, laboratory setup for CO<sub>2</sub> uptake rate.

### 4.3.1 Reactor permeability

At first, the setup is tested to evaluate the permeability. A volume of CO<sub>2</sub> is injected in the empty reactor reaching a concentration just higher than 4000 ppm and the experiment is left running to evaluate the loss of CO<sub>2</sub> over time. The result of this is shown in figure 4.3 where it is found that there is an average loss of 34 ppm/h over a period of 20 hours. This loss, however, cannot be considered constant as it decreases the more the concentration inside the reactor is equal to the concentration in the outside atmosphere. For this reason, a leakage factor is identified in order to quantify the loss of CO<sub>2</sub> for each concentration, assuming a linear relationship between the difference in concentration inside-outside and the leakage. The loss of CO<sub>2</sub> over time is calculated with equation 4.1.

$$f_r = k_r(C_{in} - C_{out}) \quad (4.1)$$

Where:

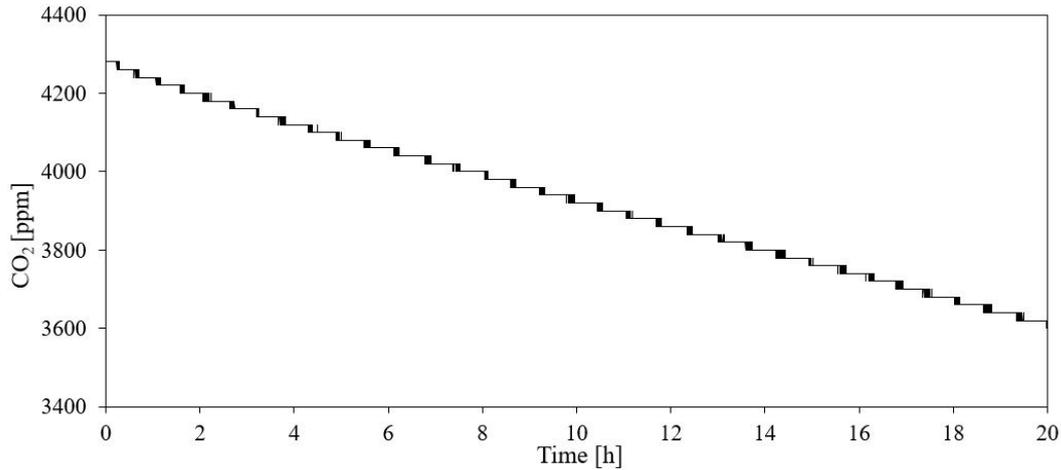
|           |   |
|-----------|---|
| $f_r$     | CO <sub>2</sub> leakage [ppm s <sup>-1</sup> ]      |
| $k_r$     | Leakage factor [s <sup>-1</sup> ]                   |
| $C_{in}$  | CO <sub>2</sub> concentration in reactor [ppm]      |
| $C_{out}$ | CO <sub>2</sub> concentration outside reactor [ppm] |

The leakage factor is found to be,  $k_r = 2.39 \times 10^{-6}$  [s<sup>-1</sup>] based on the result showed in figure 4.3 and with a constant CO<sub>2</sub> concentration of 400 ppm outside the reactor.

### 4.3.2 Test procedure

In order to avoid any pre-carbonated layer, which would result in a lower CO<sub>2</sub> uptake rate, the sample of concrete is scraped on all surfaces so to remove the carbonated layer in a range of 1 - 3 mm. By doing so, the unreacted concrete is exposed to the atmosphere mimicking a freshly cast concrete scenario. The sample is then placed in a glass jar and the CO<sub>2</sub> gas analyzer is turned on, the detector has a pump

which ensures a constant air flow.  $\text{CO}_2$  is then injected in order to reach an ideal concentration of approximately 10 000 ppm. Once the concentration falls below the room value (indicatively 400 ppm)  $\text{CO}_2$  is injected once more. The adding of  $\text{CO}_2$  happens 2 or 3 times in series for each concrete sample depending on the uptake rate. The two types of concrete are tested with this system with 1 sample for ASC (ASC1) and 2 samples for the STDC (STDC1, STDC2). The results are then evaluated based on the difference in surface area and are presented in chapter 5.



**Figure 4.3:** Permeability test in the carbonation test set-up.

#### 4.4 Alkalinity analysis

With the abrupt shut down of the laboratory due to the Covid-19 pandemic, the alkalinity test could not be performed, therefore the values are obtained from other reports where the alkalinity was measured on the same types of concrete. As for ASC, Mathiasen (2019) performed a titration test using the TitroLine Easy titrator by Schott Instruments GmbH. Based on his results, the alkalinity in terms of  $g_{\text{CaCO}_3} g_{\text{concrete}}^{-1}$  is determined. The test is performed on 6 samples and in two different acid volumes. At first the sample of concrete is dissolved in an HCl solution and a complete dissolution is observed after about 4 days. Afterwards a sample of the solution is taken and titrated with NaOH until neutralization. Following the acid-base reactions 4.2 and 4.3 and based on the difference in the amount of HCl before and after the dissolution, it is possible to determine the alkalinity.



Regarding the alkalinity of STDC, the titration test was not performed due to experimental limitations described later in section 4.6, however Vollertsen et al. (2008) have done research on the same type of concrete from the same batch, therefore the value they found is used in this report. The calculated value from the results of Mathiasen (2019) and the result of Vollertsen et al. (2008) are used in the corrosion rate calculations and the values are presented in table 4.2.

**Table 4.2:** Alkalinity of STDC from Vollertsen et al. (2008) and of ASC calculated from Mathiasen (2019).

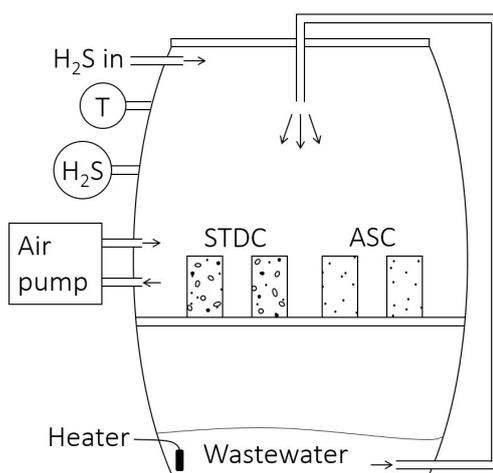
|   | STDC  | ASC   |
|---|-------|-------|
| Alkalinity<br>[ $gCaCO_3 g_{concrete}^{-1}$ ] | 0.181 | 0.402 |

## 4.5 Hydrogen sulfide test

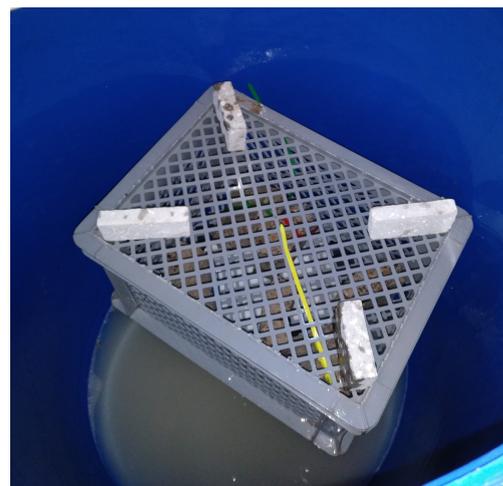
The test is performed in two controlled environments. The first is an incubator with the purpose of preparing the samples by enhancing the growth of the sulfide oxidizing bacteria. The samples are then placed in a reactor where the oxidation and adsorption rates can be more accurately calculated with the certainty that the bacteria have reached similar characteristics as in an ordinary sewer environment.

### 4.5.1 Incubator

In the incubator 4 samples of concrete, 2 of ASC and 2 for STDC are placed. The incubator consists of a sealed chamber with sensors for temperature and  $H_2S$  and the 4 samples are placed in the middle of the chamber. Wastewater from a nearby sewer is poured in the chamber and re-circulates dropping from top every 1.5 hours, in order to simulate a high moisture condition where the concrete is close to the wastewater line resulting in a heavier sulfuric acid formation, as explained in section 3.4. Re-aeration is ensured with an air pump in order to have an even distribution of the  $H_2S$  gas which is injected in the chamber every 1.5 hours. A heater is submerged in the wastewater in order to keep it at a temperature close to  $30^\circ C$  and the relative humidity is considered to be above 95%. The set-up is shown in figure 4.4 and 4.5 and ran continuously for 2 months.



**Figure 4.4:** Incubator setup sketch.



**Figure 4.5:** Concrete samples in the incubator on the beginning of the test.

### 4.5.2 Reactor

The second environment is set up just as the carbonation test presented in section 4.3 and showed in figure 4.2, with the obvious difference of using an H<sub>2</sub>S sensor instead of a CO<sub>2</sub> sensor, visible in figure 4.6. Two samples from the previous environment are tested, one for each type of concrete (STDC3 and ASC2) with the goal of measuring both adsorption and oxidation rate of H<sub>2</sub>S in order to estimate the corrosion depth over time. The samples prior to the testing are showed in figure 4.7. Since the set-up used is the same for the CO<sub>2</sub> uptake rate, in regard to leakage the two gases have different diffusion coefficients which could suggest a different leakage coefficient despite being tested under the same conditions. However, the diffusion coefficient at 25°C is approximately 5-27% higher for CO<sub>2</sub> compared to H<sub>2</sub>S (Tamimi et al., 1994; Cussler, 1997; Hvitved-Jacobsen et al., 2013) which could suggest a lower leakage factor, but since the recorded leakage for the CO<sub>2</sub> setup is relatively low at about 34 ppm per hour, the reduction in the leakage factor for the H<sub>2</sub>S reactor test is neglected.



**Figure 4.6:** Reactor setup for the H<sub>2</sub>S uptake rate measurements of ASC2 and STDC3.



**Figure 4.7:** Samples ASC2 (left) and STDC3 (right) prior to the  $H_2S$  oxidation test in the reactor after being 2 months in the incubator.

## 4.6 Experimental limitations

On the 12<sup>th</sup> of March 2020 Aalborg University and its laboratories underwent an abrupt shutdown as a preventive measure in order to contain the spread of the Covid-19 virus. For this reason the carbonation test was conducted on 1 sample ASC instead of 2 and should have also been repeated a few more times in order to better estimate the limitation of the diffusion process in this particular type of concrete. Moreover, in order to assure good permeability in the carbonation chamber, a second test should be made with little to no  $CO_2$  inside the chamber so to measure the inward leakage from outside. Regarding the  $H_2S$  test, all the 4 samples in the incubator should have been tested in the reactor, but only one sample per each type was tested due to time limitation related to laboratory shutdown. The implications of these limitation are examined in the discussion chapter.

## 4.7 Recap of testing samples

The carbonation and the  $H_2S$  test are conducted on different samples, the reason for this is the time needed to prepare the samples for the  $H_2S$  test. This is why both tests are not performed on the same samples. A recap on which samples are tested is presented in table 4.3.

**Table 4.3:** Recap of the test conducted on each sample of concrete.

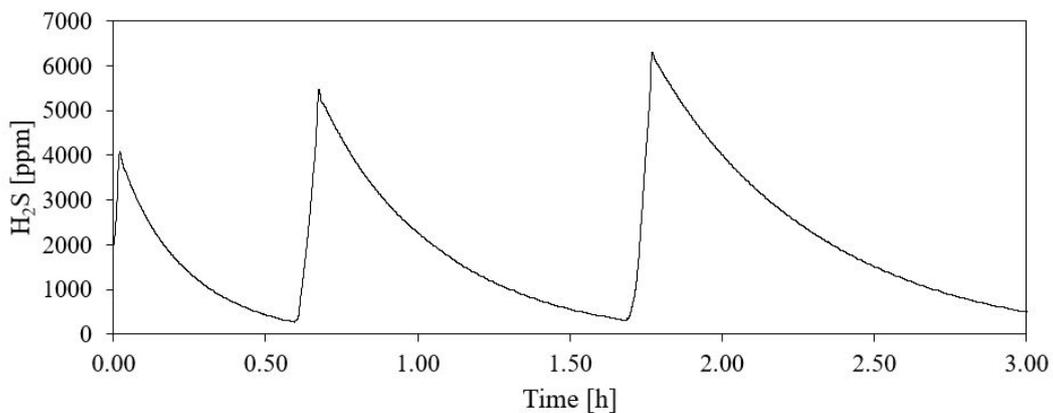
| Sample | Carbonation | H <sub>2</sub> S uptake |
|--------|-------------|-------------------------|
| STDC1  | ✓           | ✗                       |
| STDC2  | ✓           | ✗                       |
| STDC3  | ✗           | ✓                       |
| ASC1   | ✓           | ✗                       |
| ASC2   | ✗           | ✓                       |

## 5.1 Introduction

This chapter presents the results of the experiments explained in chapter 4 with the uptake of  $\text{CO}_2$  and of  $\text{H}_2\text{S}$  in both types of concrete. Moreover, the carbonation depth is found with a mathematical relationship.

## 5.2 Carbonation test

A first result showing the concentration change over time in ASC1 is shown in figure 5.1, while the results for the other samples are shown in appendix A. However, the samples have different surface area as shown in table 4.1 on page 13, therefore the  $\text{CO}_2$  absorption rate is higher when the exposed surface is higher as well. Moreover the concentration of injected  $\text{CO}_2$  in each run is slightly different as well as the minimum value reached before another injection. For this reason the results cannot be evaluated with a simple concentration-over-time curve, but on a more accurate change of concentration over time with the concentration of  $\text{CO}_2$ . Each test run is isolated and the concentration change over time ( $dC/dt$ ) is calculated. Then,  $dC/dt$  is plotted against the concentration of  $\text{CO}_2$  for each run. In order to assess for the different size of the samples, the surface specific uptake rate of  $\text{CO}_2$  is calculated in a few following steps. The slope of the change of concentration of  $\text{H}_2\text{S}$  over time is plotted and then simulated with equation 5.1. Both the measured and the simulated concentration for STDC1, STDC2 and ASC1 are shown in figures 5.2, 5.3 and 5.4 respectively.



**Figure 5.1:**  $\text{CO}_2$  uptake rate in sample ASC1 in terms of concentration over time.

$$\frac{dp_{CO_2}}{dt} = k_p p_{CO_2}^n \quad (5.1)$$

Where:

|            |   |
|------------|---|
| $p_{CO_2}$ | H <sub>2</sub> S concentration [ppm]                          |
| $t$        | Time [min]  |
| $k_p$      | Process rate constant [ppm <sup>1-n</sup> min <sup>-1</sup> ] |
| $n$        | Order of reaction [ - ]                                       |

The target of the simulation is to find the process rate constants and the order of reactions, which are needed to further calculate the surface specific CO<sub>2</sub> uptake rate in samples STDC1, STDC2 and ASC1. The simulated values are shown in table 5.1.

**Table 5.1:** Process rate constants and the reaction orders of CO<sub>2</sub> uptake in each tested sample.

| Process rates                                  | STDC1  |        |        | STDC2  |        | ASC1  |       |       |
|--|--------|--------|--------|--------|--------|-------|-------|-------|
|  | Run 1  | Run 2  | Run 3  | Run 1  | Run 2  | Run 1 | Run 2 | Run 3 |
| $k_p$<br>[ppm <sup>1-n</sup> h <sup>-1</sup> ] | 4.8e-2 | 3.6e-3 | 7.5e-4 | 6.0e-5 | 3.0e-7 | 4.68  | 2.64  | 1.92  |
| $n$<br>[ - ]                                   | 1.3    | 1.5    | 1.6    | 2      | 2.4    | 1     | 1     | 1     |

The surface specific CO<sub>2</sub> uptake rate expressed with eq. 5.2 and 5.3 can now be calculated taking into account the different dimensions of the samples. The results are presented in table 5.2 for a concentration of 500 ppm.

$$J_{CO_2} = k_F p_{CO_2}^n \quad (5.2)$$

$$k_F = k_P \frac{PV}{RT} \frac{M}{A} \quad (5.3)$$

Where:

|            |   |
|------------|---|
| $J_{CO_2}$ | Surface specific CO <sub>2</sub> uptake rate [gCO <sub>2</sub> m <sup>-2</sup> s <sup>-1</sup> ]              |
| $k_F$      | Surface specific process rate constant [gCO <sub>2</sub> m <sup>-2</sup> s <sup>-1</sup> ppmCO <sub>2</sub> ] |
| $P$        | Pressure [Pa]   |
| $V$        | Volume of gas [m <sup>3</sup> ]   |
| $R$        | Universal gas constant [m <sup>3</sup> Pa mol <sup>-1</sup> K <sup>-1</sup> ]                                 |
| $T$        | Absolute temperature [K]  |
| $M$        | Molar mass of CO <sub>2</sub> [g mol <sup>-1</sup> ]  |
| $A$        | Area of concrete exposed [m <sup>2</sup> ]  |

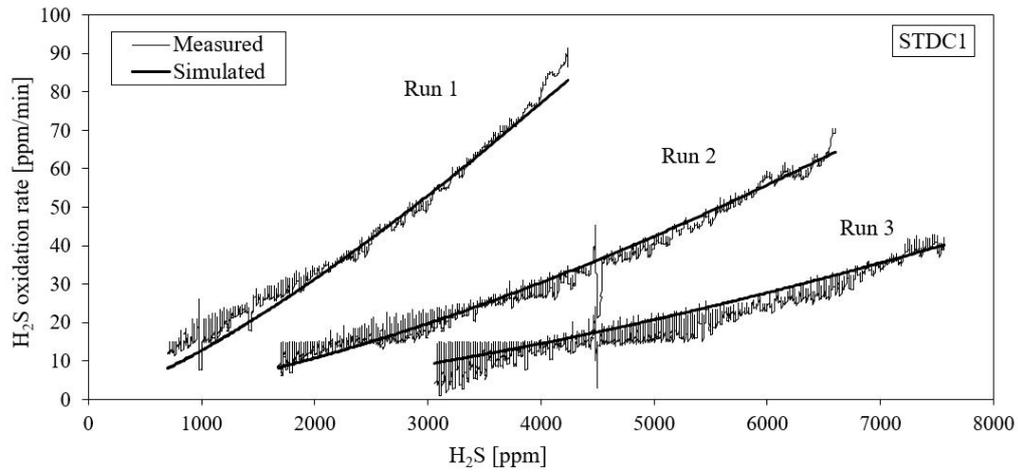


Figure 5.2: CO<sub>2</sub> uptake rate in sample STDC1.

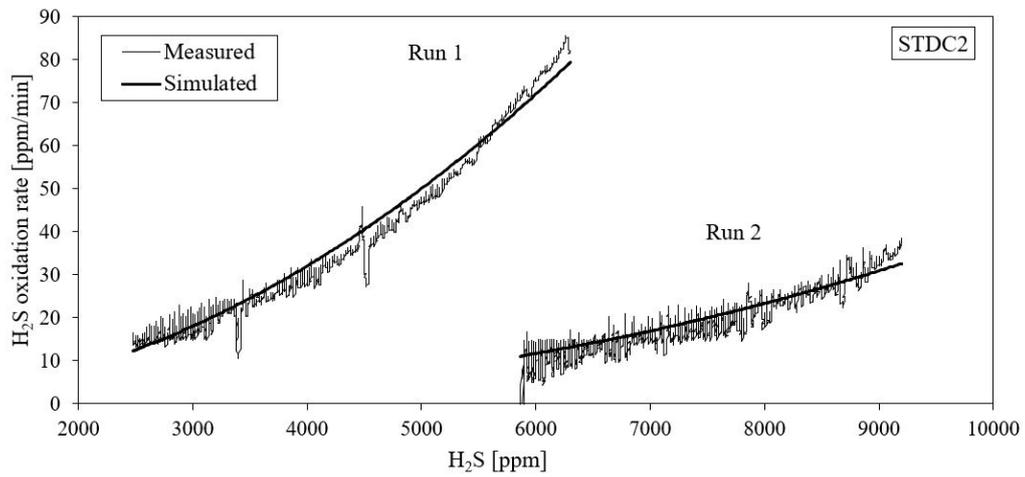


Figure 5.3: CO<sub>2</sub> uptake rate in sample STDC2.

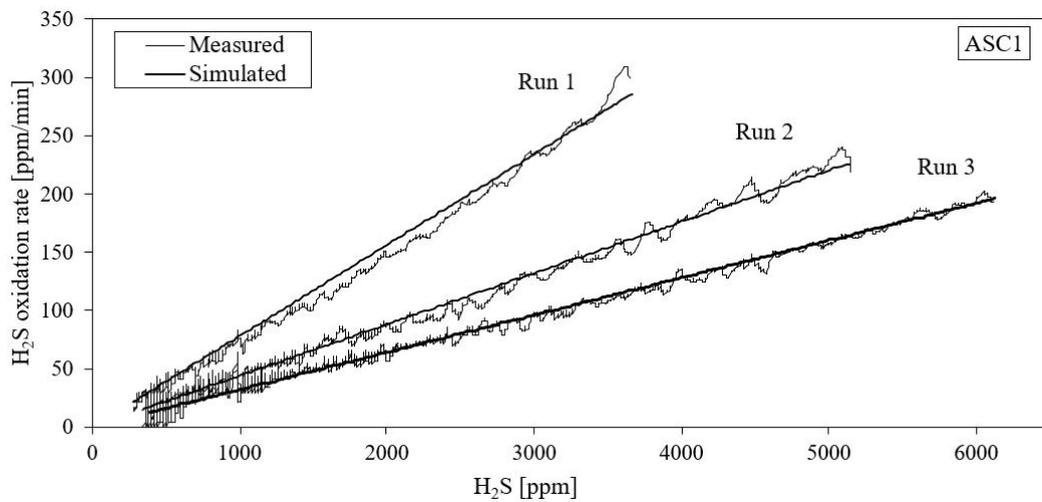


Figure 5.4: CO<sub>2</sub> uptake rate in sample ASC1.

**Table 5.2:** Average surface specific CO<sub>2</sub> uptake rate in the tested samples at a concentration of 500 ppm.

|  | STDC1 | STDC2 | ASC1 |
|--|-------|-------|------|
| $J_{CO_2, r^{500}}$<br>[mg m <sup>-2</sup> min <sup>-1</sup> ] | 0.24  | 0.027 | 5.86 |

The comparison between figure 5.2 with figures 5.3 and 5.4 shows a clear higher rate of CO<sub>2</sub> uptake in ASC1 than the standard concrete samples. This can also be seen more precisely in table 5.2 where the surface specific uptake rates are shown for a concentration of 500 ppm. The rate of ASC1 compared to STDC1 and STDC2 is 24.4 and 215 times higher respectively. The ratio between ASC1 and STDC2 seems overwhelmingly high and might be a result of the carbonated layer not being thoroughly removed from sample STDC2, thus this result is disregarded from any further calculation and analysis.

### 5.2.1 Carbonation depth

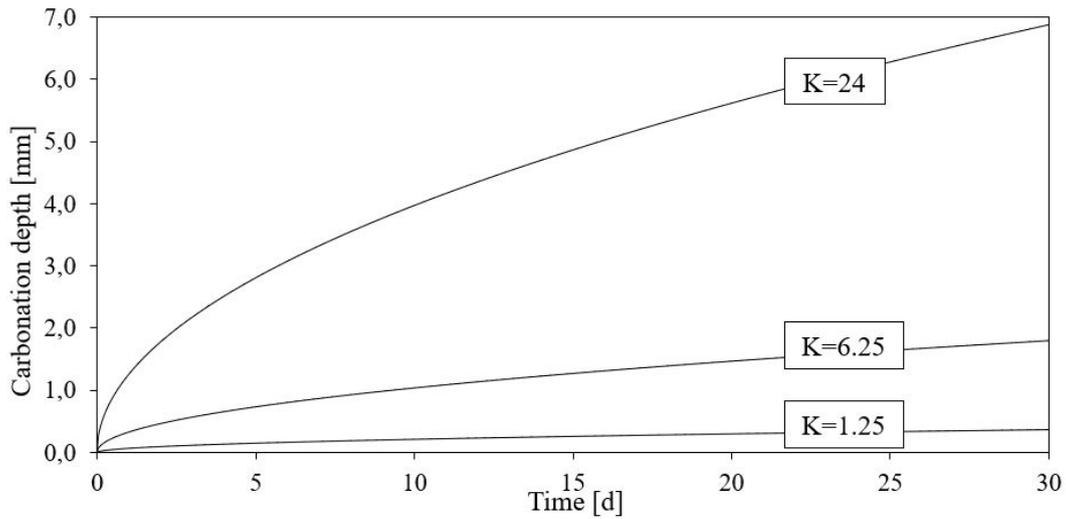
As mentioned in chapter 2, carbonation is chemical process that diffuses into the concrete. Knowing the relationship between carbonation front and time can be useful in reinforced concrete in predicting loss of mechanical strength, particularly in the steel bars (Jung et al., 2011), but also in understanding the decrease rate of surface pH which can be a good indicator for the beginning of the microbial induced corrosion. The depth of the carbonated layer over time can be estimated with Fick's laws of diffusion and it is commonly simplified as shown in equation 5.4 (Sisomphon and Franke, 2007; Mcpolin et al., 2007; Torres et al., 2017).

$$x = K\sqrt{t} \quad (5.4)$$

Where:

|     |  |
|-----|--|
| $x$ | Carbonation depth [mm]                           |
| $K$ | Carbonation coefficient [mm yr <sup>-0.5</sup> ] |
| $t$ | Time [yr]  |

The carbonation coefficient is not actually constant because the porosity in the carbonated layer changes with time and depends also on atmospheric parameters such as temperature, but due to the slowness of the process it can be considered constant (Mcpolin et al., 2007). Lagerblad (2005) suggests values for CEM I concrete (one of the most widely used concretes similar to the STDC type of this study) in the order of  $K = 1\text{-}5 \text{ mm yr}^{-0.5}$  found under typical Nordic climate for unpainted concrete in the outdoor, also confirmed by Monteiro et al. (2012). Assuming a linear relationship between carbonation depth and CO<sub>2</sub> concentration and a minimum CO<sub>2</sub> concentration of 500ppm in the sewers (Hvitved-Jacobsen et al., 2013), the  $K$  factor can be re-scaled to 1.25-6.25 mm yr<sup>-0.5</sup>. As mentioned before, it is found that the uptake of CO<sub>2</sub> is approximately 24 times higher in ASC, therefore the corresponding carbonation coefficient,  $K$ , is upscaled accordingly resulting in a minimum coefficient  $K = 24 \text{ mm yr}^{-0.5}$ . The expected carbonation depths over time based on equation 5.4 are shown in figure 5.5 for both STDC and ASC.



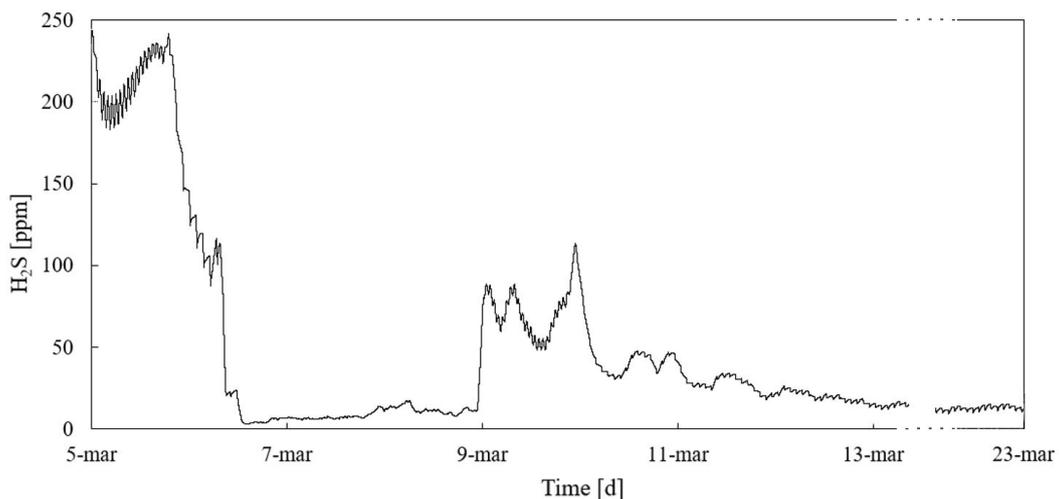
**Figure 5.5:** Expected carbonation depth for STDC and ASC, over the period of 30 days.

Knowing that ASC is applied in a layer of width between 10-12 mm, based on the above relations and results the layer is assumed to be fully carbonated in a period between 2 and 3 months.

## 5.3 Hydrogen Sulfide test

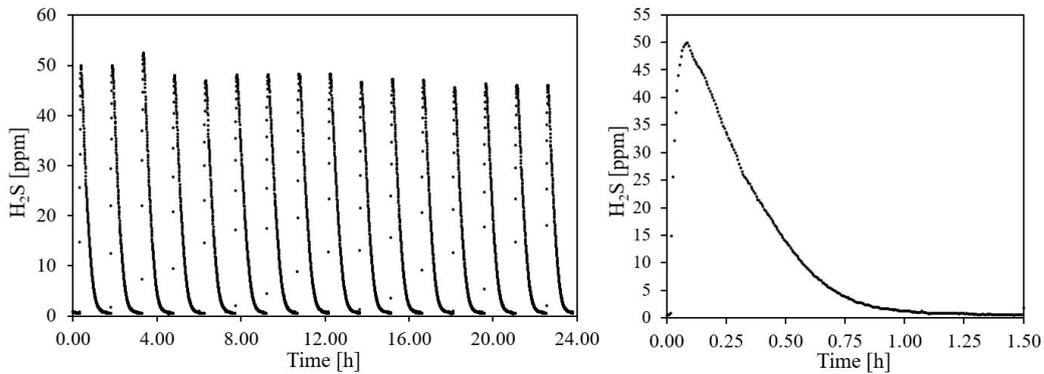
### 5.3.1 Incubator

The set-up began running on the 5<sup>th</sup> of March and ended on the 5<sup>th</sup> of May. Since the beginning of the test, stable conditions were achieved after about 8 days and continued for 53 days. Figure 5.6 shows the concentration over time of H<sub>2</sub>S in the set-up (as an 8 min moving average for a better visualisation).



**Figure 5.6:** Moving average (8 min) of the concentration change over time in the H<sub>2</sub>S uptake set-up in a span of approximately 18 days.

The  $\text{H}_2\text{S}$  concentration is measured every 20 seconds with the gas being injected every 1.5 hours. Figure 5.7 shows a daily measurement during stable conditions, together with the first injection cycle of the same day.



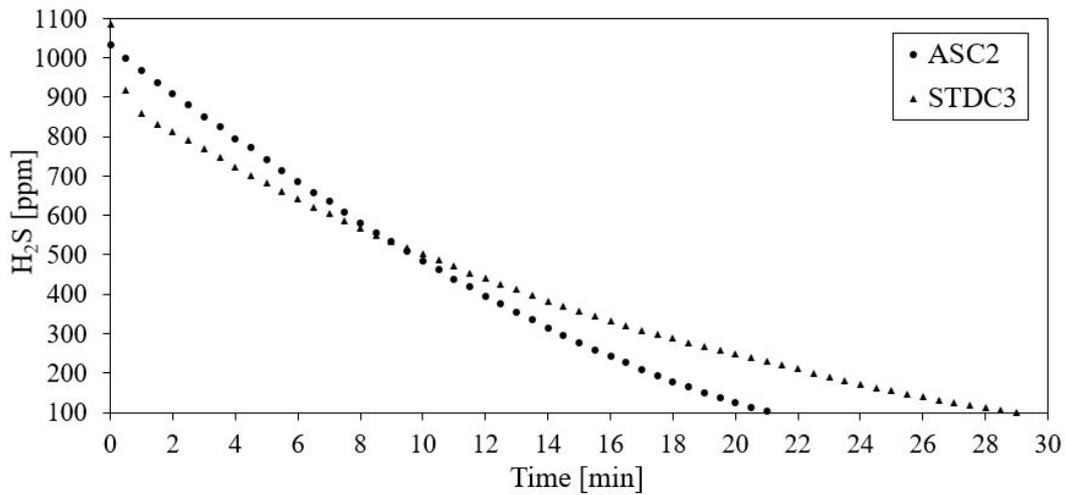
**Figure 5.7:**  $\text{H}_2\text{S}$  measurement on the day of March 19<sup>th</sup> during stable conditions, with the graph on the right focusing on the first cycle of the day.

The decrease of concentration visible particularly in the right side graph is relatively rapid for a few of reasons. The decrease is attributed not only to the oxidation on the concrete samples' surfaces, but also on the adsorption both on the samples as on the incubator walls and in the air circulation system. Nielsen et al. (2008) found that the adsorption and oxidation on the plastic surfaces is approximately two orders of magnitude lower compared to concrete. This factor combined with the wastewater exchange equilibrium and the loss by diffusion out of the incubator contribute to the rapid decrease of  $\text{H}_2\text{S}$  in the gas phase.

After a period of 2 months a sample for each type of concrete undergoes an  $\text{H}_2\text{S}$  uptake rate test performed in a smaller chamber showed in figure 4.2 on page 15 used for the carbonation test, the results are presented in the next section.

### 5.3.2 Reactor

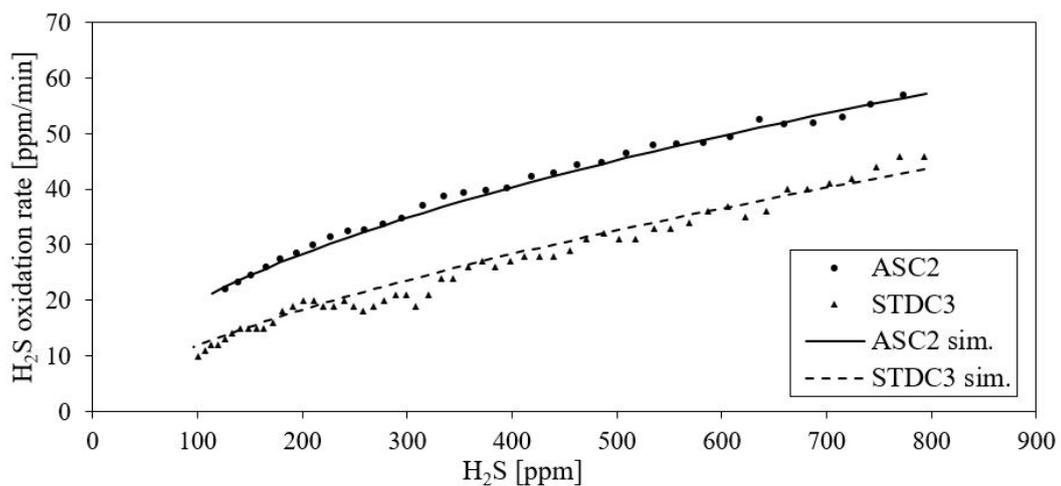
One sample of each type of concrete is tested in order to establish the uptake rate of  $\text{H}_2\text{S}$ . The change of concentration over time is shown in figure 5.8, where concentrations below 100 ppm are not shown due to possible sensor inaccuracy, and the measurements are used to calculate the  $\text{H}_2\text{S}$  absorption rate on the concrete surface which ultimately leads to the estimate of the corrosion rates presented in the following section 5.4.



**Figure 5.8:** Concentration change of  $\text{H}_2\text{S}$  over time observed in the experiment in the reactor for ASC2 and STDC3.

## 5.4 Corrosion rates

The estimate of corrosion is done with a model consisting of two equations, the first one calculates the flux of  $\text{H}_2\text{S}$  through the concrete surface and the second calculates the average corrosion per time. In the case of this report the flux of  $\text{H}_2\text{S}$  is derived from the results of the second  $\text{H}_2\text{S}$  experiment explained in section 4.5.2 on page 18 and showed in figure 5.8. The procedure to determine the surface specific  $\text{H}_2\text{S}$  oxidation rate uses the same approach as in section 5.2 on page 21 and 22 when determining the  $\text{CO}_2$  uptake rate.



**Figure 5.9:** Oxidation rate of both types of concrete with the corresponding simulated rates.

**Table 5.3:** Process rate constants and the reaction orders of H<sub>2</sub>S uptake in each tested sample.

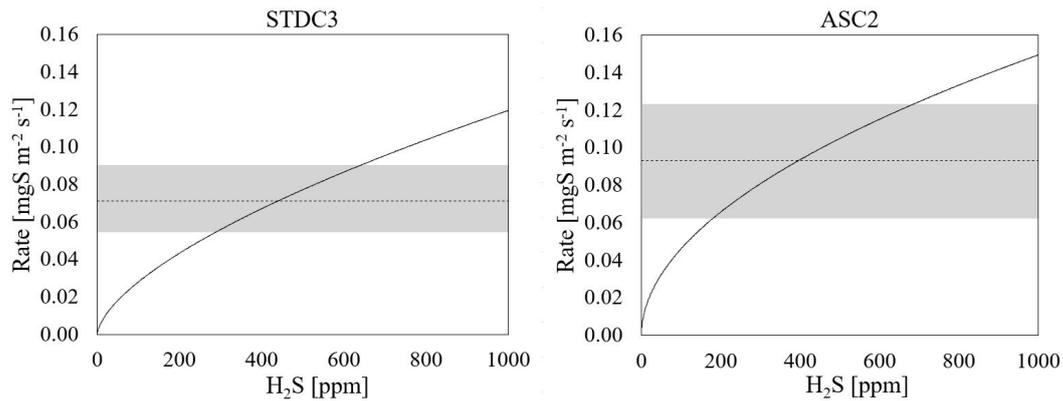
|       | $k_p$<br>[ppm <sup>1-n</sup> min <sup>-1</sup> ] | n<br>[ - ] |
|-------|--|------------|
| STDC3 | 0.65   | 0.63       |
| ASC2  | 1.9  | 0.51       |

It is clear that the rate of oxidation is not proportional to the concentration of H<sub>2</sub>S, therefore the surface specific H<sub>2</sub>S oxidation rates are calculated for 10, 100 and 500 ppm with equations 5.2 and 5.3, with the relative parameters of H<sub>2</sub>S and of samples STDC3 and ASC2. The results are presented in table 5.4.

**Table 5.4:** H<sub>2</sub>S oxidation rates in STDC3 and ASC2 samples.

|                  | STDC3<br>[mg m <sup>-2</sup> s <sup>-1</sup> ] | ASC2<br>[mg m <sup>-2</sup> s <sup>-1</sup> ] |
|------------------|--|---|
| J <sub>10</sub>  | 0.007  | 0.014   |
| J <sub>100</sub> | 0.028  | 0.046   |
| J <sub>500</sub> | 0.077  | 0.105   |

The above findings for STDC3 are in line with the findings from Vollertsen et al. (2008) which have done numerous tests with concrete of the same batch. Figure 5.10 shows the removal rate of H<sub>2</sub>S in the reactor for both samples based on concentrations up to 1000 ppm.

**Figure 5.10:** Removal rate of H<sub>2</sub>S in the reactor for STDC3 (left) and ASC2 (right) together with 25-75% percentile (grey area) interval and the median value (dashed line).

### 5.4.1 Corrosion rates at constant concentrations

Once the surface specific H<sub>2</sub>S oxidation rates are calculated, it is possible to estimate the corrosion rates in terms of lost concrete or with minimal structural capacity. The average rates are estimated with equation 5.5, where the term 100/32 refers to the simplification that 32 g of combined sulfur are needed in order to produce the acid which corrodes 100 g of concrete expressed as CaCO<sub>3</sub>. The alkalinity values for STDC3 and ASC2 are 0.181 and 0.402 gCaCO<sub>3</sub> g<sub>concrete</sub><sup>-1</sup> respectively.

$$C = \frac{100}{32} \frac{J_S}{A} \frac{1}{d} k \quad (5.5)$$

Where:

|       |   |
|-------|---|
| $C$   | Average annual corrosion rate [mm yr <sup>-1</sup> ]                                    |
| $J_S$ | Surface specific H <sub>2</sub> S oxidation rate [g mm <sup>-2</sup> yr <sup>-1</sup> ] |
| $A$   | Alkalinity of the concrete [gCaCO <sub>3</sub> g <sub>concrete</sub> <sup>-1</sup> ]    |
| $d$   | Concrete density [g mm <sup>-3</sup> ]  |
| $k$   | Corrosion reduction factor [ - ]  |

The above presented equation is valid under certain assumptions and must be evaluated accordingly. The equation is originally presented by Pomeroy et al. (1974) and has later been used in many other reports and design manuals (Sanders et al., 1989; Bowker et al., 1992). First of all, the corrosion rate is an average value, not accounting for the difference in corrosion rates which are higher in the crown and on the side walls near the wastewater line as explained in section 3.4 on page 11. The aggregates present in the concrete are considered as non-reactive to the attack of sulfuric acid (inert), however some of the aggregates do react with the acid thereby lessening the corrosion rate.

In regard to the production of acid, findings from Nielsen et al. (2014) suggest that the higher the concentration of H<sub>2</sub>S, the lower the corrosion reduction factor, therefore a different factor is applied to each tested concentration.

Knowing the assumptions and simplifications, the corrosion rates for STDC3 and ASC2 at constant H<sub>2</sub>S concentrations of 10, 100 and 500 ppm are presented in table 5.5, while table 5.6 shows the time it would take for a layer of 10 mm to be corroded. This last result is provided because the ASC concrete when sprayed should produce a coating layer of 10-12 mm. Additionally, based on the previous assumption that all the H<sub>2</sub>S is oxidise, the corrosion reduction factor for the three concentrations are:  $k_{10} = 0.5$ ,  $k_{100} = 0.4$ ,  $k_{500} = 0.3$ . The relevancy of the results and the assumptions made are discussed in chapter 6.

|       | $C_{10}$               | $C_{100}$ | $C_{500}$ |
|-------|------------------------|-----------|-----------|
|       | [mm yr <sup>-1</sup> ] |           |           |
| STDC3 | 0.77                   | 2.63      | 5.44      |
| ASC2  | 0.91                   | 2.35      | 4.01      |

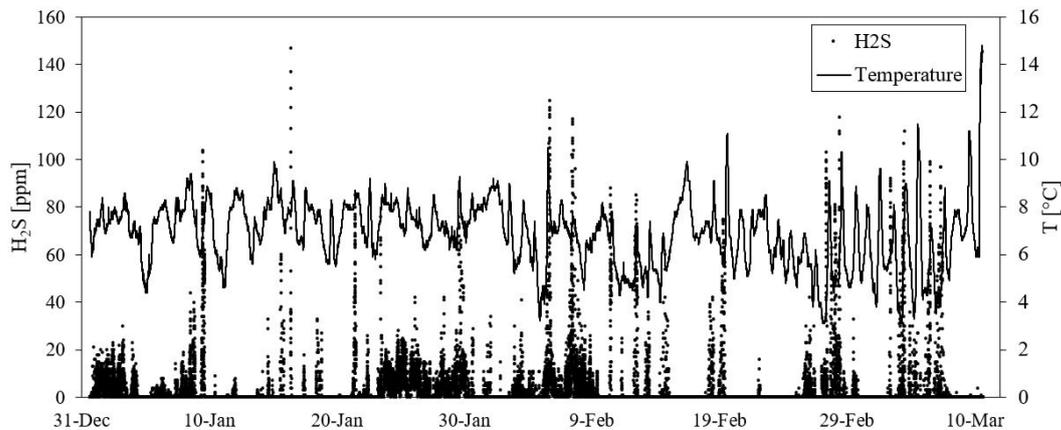
**Table 5.5:** Corrosion rates in samples STDC3 and ASC2 at different H<sub>2</sub>S concentrations.

|           | $t_{10mm}$ [yr] |      |
|-----------|-----------------|------|
|           | STDC3           | ASC2 |
| $C_{10}$  | 13              | 11   |
| $C_{100}$ | 3.8             | 4.3  |
| $C_{500}$ | 1.8             | 2.5  |

**Table 5.6:** Time in order for a layer of 10 mm of concrete to be corroded.

### 5.4.2 Corrosion rates at varying concentrations

Previously, in section 1.1 of the introduction it was mentioned that the ASC type concrete has been installed outside the wastewater treatment plant of the town of Ikast. At the same location, H<sub>2</sub>S measurements were done at a manhole downstream of a pressure main with measurements every 5 min from the 31.12.19 to 11.03.20 for a total 70 days, shown in figure 5.11 together with the temperature variations. Based on this information, a method is developed to estimate the yearly corrosion rate at this specific location. The rate of corrosion found is valid only in the concrete portions closest to the pressure main outlet, thus being the most critical.



**Figure 5.11:** H<sub>2</sub>S and temperature measurements over 70 days the in a manhole at the test location in the town of Ikast.

The corrosion rate calculation follows the same procedure as before with the difference that the H<sub>2</sub>S concentration varies with time. A 365 days series is developed from the 70 days series taking into account the yearly change in temperature and an additional overall increase in temperature of +2°C following scenario RCP8.5 of IPCC (2014). This scenario is the most critical in the report and an increase of +2°C is the average of the indicated possible values in scenario RCP8.5, valid from 2046 to 2065. The focus on the temperature increase is related with the direct correlation of biological activity. Sanders et al. (1989) and other studies suggest and increase in the sulphide generation rates of 7% for each 1°C increase in temperature. Thus, the

H<sub>2</sub>S concentration has been proportionally increased for each season, starting with a minimum of 7°C in winter and a maximum average of 20°C in summer.

The above time series does not show a constant or semi-constant concentration, but instead an intermittent one as a result of the on-off time of the wastewater pumps. It is assumed that there is no decay of the biomass when the H<sub>2</sub>S reaches 0 ppm and thus there is no lag in the beginning of the oxidation once the concentration of H<sub>2</sub>S rises again.

A simulation is then setup with the MATLAB R2019b software taking into account all of the above and re-calculating the oxidation rate and the corrosion depth for every concentration at each time step and assuming that all the recorded H<sub>2</sub>S is oxidized. The full time series can be seen in appendix B. Contrary to the previous scenario of a constant concentration throughout the year, the corrosion reduction factor is assumed,  $k = 1$ . A rate of corrosion of 0.91 mm yr<sup>-1</sup> is found and the total time for a 10 mm layer of ASC2 to be fully corroded is then calculated at 10.9 years.



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## 6.1 Carbonation

It is found, based on the simulation of the measurements, that the uptake of CO<sub>2</sub> is about 24 times higher in ASC1 compared to STDC1. The result does not come as a surprise as it is expected for the ASC type to carbonate faster for two reasons. The first is the higher porosity which is directly related to the water-to-cement ratio (w/c). The company that created the ASC type, Marlon Tørmørtel A/S, state that the w/c ratio is 0.5. The ratio for the STDC type is unknown, but since it is a common concrete and its density is also equal to many other common concrete types, the w/c for STDC can be assumed between 0.3 and 0.4. Therefore, the porosity is higher in ASC than STDC, thereby permitting more CO<sub>2</sub> to penetrate deeper and faster. Another aspect to consider is the fact that STDC contains aggregates of a larger size as visible when comparing the samples in figure 4.1 on page 14. The aggregates have a higher density than the cement paste resulting in smaller pores, for this reason the carbonation process is even slower.

### Diffusion limitation

The rate at which CO<sub>2</sub> (and therefore carbonation) penetrates into the concrete is heavily influenced by diffusion. The deeper the layer the harder it is for the CO<sub>2</sub> to penetrate, hence the advance of the carbonated front decreases with time. This has been taken into account with n<sup>th</sup> order kinetics using n=0.5, but in reality the number might be even lower as a substantial decrease in the uptake rates was observed after each run. Probably with more runs it is possible to estimate the order of reaction with more accuracy, also in relation to the different porosity in the two types of concrete.

### Applications of ASC

If the ASC is implemented in connection with reinforced concrete, this will represent a risk for the mechanical strength of the structure as the rebar will begin to corrode once it comes in contact with the carbonation front. However, the main objective of this report is to evaluate the capacity of ASC in reducing the MIC corrosion issue and in this regard, the high carbonation rate is considered a positive aspect when related to the decrease of pH.

### pH decline

As the pH drops, the surface of the concrete is colonized by bacteria which oxidize H<sub>2</sub>S producing sulfuric acid. Normally, a high pH would be advised to prevent

corrosion and this is true, as the bacteria would not be able to grow. However, this would result in a build up of  $H_2S$  which would cause not only odour problems, but the gas would travel to other portions of the sewer network causing massive corrosion down the line where the pipes have already been colonized by the bacteria. The rapid drop in pH, then, promotes fast colonization by  $H_2S$  oxidizing bacteria thereby reducing the concentration of  $H_2S$  shortly after the concrete has been installed. On the other hand, sulfuric acid is also rapidly produced shortly after the placement of ASC and the effectiveness in containing the corrosion rates is discussed in the next section.

## 6.2 Corrosion: constant $H_2S$ concentration

Considering a scenario where the  $H_2S$  concentration is constant, the yearly rate of corrosion below 100 ppm is similar for both ASC and STDC, however the oxidation rates are almost twice higher in ASC. In a lower range of concentration, the results indicate that the two types of concrete behave in a similar way in terms of corrosion rate, while the difference in oxidation rate is significant. This suggests that an ideal sewer section that is coated with ASC can reduce the concentration of  $H_2S$  twice as fast and thus reduce the corrosion related problems downstream, with the downside that the coating of 10-12 mm needs to be replaced on average every 4 to 11 years. At a concentration of 500 ppm the corrosion rate is 38% higher in STDC and the oxidation rate is about 27% lower than ASC. This shows that in terms of corrosion rates, the ASC performs better than STDC at higher  $H_2S$  concentrations while the oxidation rate remains higher, but with a lower proportion if compared to concentrations below 100 ppm. At constant 500 ppm a layer of 10 mm of ASC corrodes in about 2.5 years, indicating that this type of concrete could not represent a valid option at reducing the corrosion rates in a sewer network where such high concentrations are constantly registered. It must be clarified, however, that such high constant concentration is rarely recorded in the sewers. On the other hand, it proves a good tool in constant concentrations below 100 ppm, because even though the coating layer needs to be replaced every 4 to 11 years, the section that needs to be repaired is significantly shorter, thereby reducing the maintenance costs.

### Corrosion reduction factor

A corrosion reduction factor is applied to the corrosion rate equation at different  $H_2S$  concentrations. The reason for this is that findings from Nielsen et al. (2014) show that only 30-90% of the sulfide is actually oxidized to sulfuric acid and the percentage is inversely proportional to the exposure time of the concrete to  $H_2S$ . The explanation to this phenomenon is probably related to elemental sulfur being an intermediate step. Both H. S. Jensen (2009) and Nielsen et al. (2014) recorded that when the  $H_2S$  concentration drops to zero, the corrosion process continues for a certain time. They observed a continuing decrease in the oxygen in the atmosphere, suggesting that the oxidation of sulfide has elemental sulfur as an intermediate step, which is oxidized once the concentration of  $H_2S$  drops. Therefore, when the concentration remains constant there is a continuous build up of elemental sulfur

which is not oxidized until the concentration of H<sub>2</sub>S in the atmosphere drops to zero. More specifically, Nielsen et al. (2014) recorded a continuous mass loss in the concrete after the depletion of H<sub>2</sub>S which accounted for 25-75% of the total mass loss. The rate of post-corrosion and the correlated time seem to be proportional to the exposure time. A confirmation of the build up of elemental sulfur could be inferred from sample ASC2 after being for 2 months in a sewer-like environment (the incubator), shown in figure 6.1, where the yellow-ish color could indicate the presence of elemental sulfur and the black area could indicate the precipitation of iron sulfide (FeS).



**Figure 6.1:** Sample ASC2 after being 2 months in the incubator.

### H<sub>2</sub>S oxidation

When calculating the corrosion rate with equation 5.5 on page 29 it is assumed that all the H<sub>2</sub>S in the atmosphere is oxidized on the surface wall, but only part of it contributes to the production of acid. The first assumption is not entirely true as the due to natural ventilation it is inevitable that some of the gaseous H<sub>2</sub>S escapes the system and is not oxidized. Additionally, the concentration of H<sub>2</sub>S in the gas phase is dependant on the concentration in the water phase, therefore the higher the uptake from the concrete the higher will be the release from the wastewater. In this regard, under steady state conditions, the release of H<sub>2</sub>S from the wastewater will be higher when ASC is used due to the higher uptake rate. The result of this is a further decrease in the concentration of H<sub>2</sub>S in the atmosphere in the downstream sections of the pipe. The uptake rate of H<sub>2</sub>S on the concrete is relatively fast compared to the release rates from the wastewater, therefore it will probably not be changed based on the H<sub>2</sub>S concentration in the gas phase, for this reason, given that the density of concrete is generally similar, the most limiting factor in the corrosion rate is the alkalinity.

### **Diffusion limitation**

It is also worth mentioning that the corrosion rate can decrease in time due to a diffusion limitation through the corroded layer. Corroded concrete often results in gypsum which may or may not remain attached to the pipe depending on how frequently the wastewater line changes. In the case of gypsum remaining attached to the concrete, a buffer zone is then present because the sulfuric acid produced on the surface has to penetrate the gypsum layer first in order to attack the concrete. It is obvious then how a deeper corroded layer, if still attached to the concrete, can progressively slow down the corrosion process (Apgar et al., 2007). The impact of this aspect has not been evaluated and should be investigated in order to establish the magnitude of the reduction, especially in scenarios with more constant wastewater flow.

### **6.3 Corrosion: varying H<sub>2</sub>S concentration**

In order to have more reliable results in the concrete downstream of a pressure main at Ikast, a 70 days concentration time series has been used. The model used to estimate the corrosion rates includes both conservative and non-conservative assumptions. The corrosion rates found apply only for the closes concrete sections to the pressure pipe outlet and this has been done in order to evaluate the most critical scenario.

#### **Wastewater temperature**

A temperature variation has been applied to the series and the H<sub>2</sub>S concentration has been increased accordingly, with a minimum wastewater temperature of 7°C and a maximum of 20°C. The minimum temperature originates from an average of the temperature measured in the time series in the atmosphere, while the maximum is inferred based on general knowledge of sewer temperatures. The assumed increase in temperature during the season is probably overestimated in this specific case, because the wastewater lies in the pressure pipe for a certain amount of time, thus its temperature decreases. Research made by Sallanko and Pekkala (2008), at a similar climate to the one of Denmark, found that the decrease of household wastewater temperature during summer in a pressure main can be up to 1.06°C per hour. Therefore, it is likely that the temperature of the wastewater released from the pressure main is lower than the average temperatures of wastewater in gravity pipes, but in absence of more precise data and in order to keep a conservative approach, the temperatures have been assumed similar to the ones of wastewater in gravity sewers.

#### **H<sub>2</sub>S oxidation**

One more assumption is that all the H<sub>2</sub>S present is oxidized. This is not entirely true as some of the gas will naturally be lost due to the natural ventilation, but this loss can be hard to quantify and in order to maintain a conservative, it was assumed that all the H<sub>2</sub>S would be oxidized thereby overestimating the corrosion rates. However, the oxidation of H<sub>2</sub>S is a rather quick process as the results from the laboratory experiment on the ASC2 sample in section 5.3 on page 25, where

about 1000 ppm where oxidized in less than 25 minutes, therefore it can be assumed that all the  $\text{H}_2\text{S}$  is immediately oxidized. It is also worth noting that the ratio of gas volume to concrete area in the reactor can be even twice as high in a sewer, thereby reducing the  $\text{H}_2\text{S}$  more rapidly than what is observed in the reactor.

### **Corrosion reduction factor**

The corrosion reduction factor,  $k$ , in this case has been considered equal to 1, meaning that there is no reduction of corrosion rate. The reason for this lies in the intermittent  $\text{H}_2\text{S}$  concentration. As explained before, elemental sulfur could clearly be an intermediate product before the production of sulfuric acid and part of it is immediately oxidized while another part is stored. When the  $\text{H}_2\text{S}$  drops to zero, the stored sulfur is oxidized, but if the concentration remains constant this will not happen. This means that during the times when there is no  $\text{H}_2\text{S}$ , the stored sulfur is oxidized and therefore all the oxidized sulfur leads to sulfuric acid. Then, in the case of a force main, where the wastewater flow is intermittent, so is the concentration of  $\text{H}_2\text{S}$  allowing for all of the elemental sulfur to be oxidized without any reduction of corrosion due to stored sulfur.

### **Adsorption**

Additionally, one of the cause of the decrease in  $\text{H}_2\text{S}$  concentration could be the adsorption on the pipe walls, leading to an overestimation of the oxidation rate. On this matter, H. S. Jensen (2009) suggests that it could still be oxidized once the  $\text{H}_2\text{S}$  in the atmosphere is depleted, which supports the theory of the production of sulfuric acid for a certain amount of time after  $\text{H}_2\text{S}$  in the atmosphere has depleted.

### **Bacterial decay**

It can be argued that when the concentration goes to zero, provided that  $\text{H}_2\text{S}$  is the only limiting factor, the acid producing bacteria start decaying, thereby resulting in a lag in the acid production once the  $\text{H}_2\text{S}$  concentration rises again. However, research from H. S. Jensen (2009) shows that even after 6 months of starvation, it took only 18 hours of  $\text{H}_2\text{S}$  exposure for the biological activity to reach 80% of its full capability. For this reason it is assumed there is no lag between the increase in  $\text{H}_2\text{S}$  and the beginning of oxidation, also because the longest period of starvation during the recorded series is just 6.7 days.

## **6.4 Samples testing**

The corrosion rates for samples ASC2 and STDC3 rely heavily on the  $\text{H}_2\text{S}$  oxidation rate. This rate has been calculated based on just one measurement per each sample. The reason for this is the sudden shutdown of the laboratories, therefore all the corrosion rates must be evaluated keeping in mind that only one sample per each type of concrete was tested with only one run. Unfortunately no more tests could be performed, nonetheless the oxidation rates are in range with other studies so, while

it is advisable to repeat the test on other samples in order to confirm the results, the calculated rates are believed to be in a correct range.

### **6.5 Machinery, installation and maintenance**

The results of the report, regarding the ASC type concrete, rely on the hypothesis of an even distribution of the material on the sewer walls maintaining intact the sewer design criteria. The inner coated walls are assumed to be smooth and even throughout the entire pipe promoting a steady unobstructed wastewater flow. Based the H<sub>2</sub>S measurements at the specific location, the section immediately downstream of the force main would require a new coating every 11 years and in the worst case scenario, with a constant concentration of 500 ppm, about every 2.5 years. However, no matter the concentration, even supposing that a new coating is needed every year, this could still be a positive result considering that thanks to the spraying machine there is non need to dig up the pipe and the re-coating operation should be relatively quick. For these reasons, the maintenance costs are presumed to be low compared to conventional maintenance procedures.

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The potential to reduce sulfuric acid corrosion damages and preserve concrete in the sewers with and alkaline shotcrete (ASC) has been evaluated in a series of steps. Laboratory experiments were conducted on two types of concrete, an experimental one and a standard type (STDC) commonly used in Denmark. The chemical process of carbonation is estimated and it is found that the process is significantly quicker for ASC compared to STDC. The result, when related to a pH drop, is considered positively in the aspect that bacterial growth is promoted, thereby reducing the concentration of hydrogen sulfide ( $\text{H}_2\text{S}$ ) more rapidly. Samples of both types of concrete were incubated for 2 months in a sewer-like environment and later the uptake rate of  $\text{H}_2\text{S}$  was measured. It was found that at  $\text{H}_2\text{S}$  concentrations below 40 ppm, the uptake rate is twice as high in ASC and the ratio decreases with increasing  $\text{H}_2\text{S}$  concentration. Based on the surface specific  $\text{H}_2\text{S}$  oxidation rates, the yearly average corrosion was estimated finding that at concentrations below 100 ppm both concretes behave in the same way, with a 10 mm layer being corroded in approximately 4 years. A more specific evaluation of the corrosion rates was made with data from a manhole immediately downstream of a pressure main outside the wastewater treatment plant of Ikast, where heavy corrosion has been reported. It was found that the corrosion rates for ASC are approximately  $0.9 \text{ mm yr}^{-1}$  and a coating layer of 10 mm will thereby fully corrode in 11 years. Overall, even though both concretes behave in a similar way in terms of corrosion rates, the capability of the ASC to oxidize significantly higher amounts of  $\text{H}_2\text{S}$  is believed to of grate value because this results in more  $\text{H}_2\text{S}$  being released from the wastewater in the parts of the pipeline coated with ASC. In this regard, the coated section will require a high degree of maintenance, but it will also preserve the concrete sections downstream as the  $\text{H}_2\text{S}$  concentration will be lower both in the gas and in the liquid phase. Combining this aspect with a supposed ease of re-coating, thanks to the concrete spraying machine, it is believed that the ASC type concrete is an effective tool in preserving the concrete in the sewers and in keeping the maintenance costs relatively low.



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# Appendix



# Appendix A - Carbonation

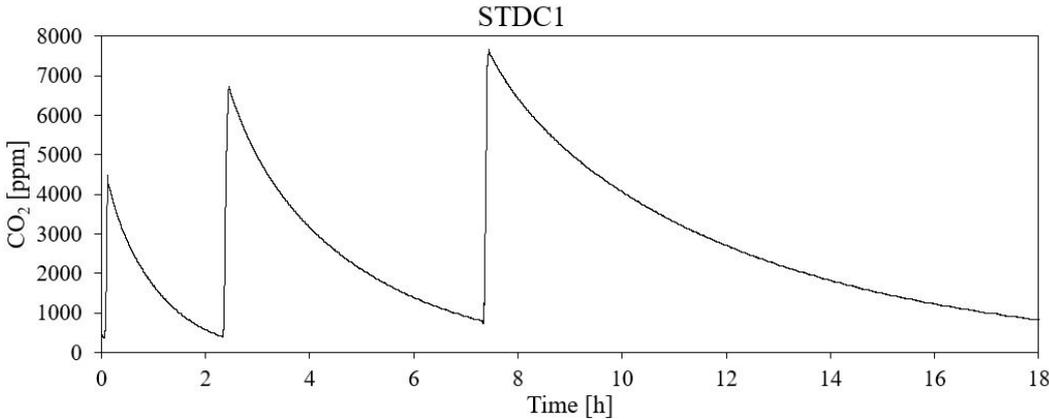


Figure 1: CO<sub>2</sub> uptake rate in sample STDC1 in terms of concentration over time.

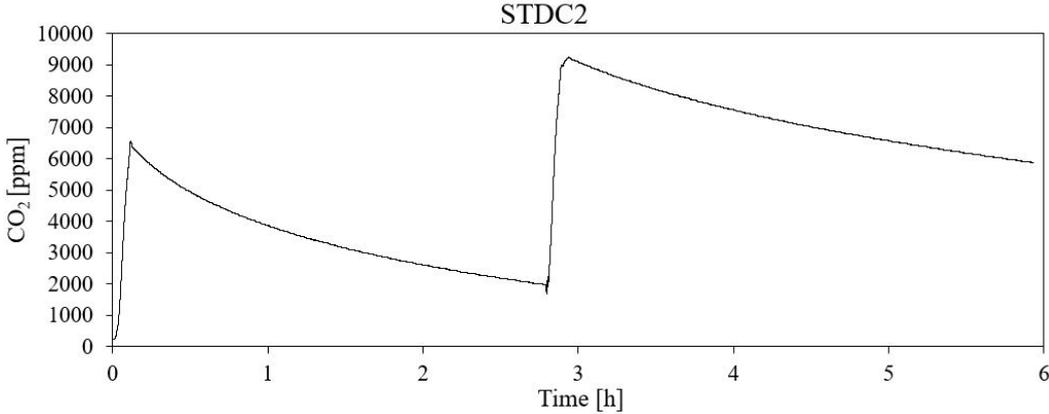


Figure 2: CO<sub>2</sub> uptake rate in sample STDC2 in terms of concentration over time.



## Appendix B - Yearly corrosion rate simulation

The yearly corrosion rate at varying concentrations is simulated based on a 70 days series of measurements every 5 minutes. Considering a total of 22 804 single measurements, the series presents a good variability and is therefore used as a basis for a 350 days period with the H<sub>2</sub>S concentration adjusted based on temperature variations. The series is shown in the next page in figure 3.

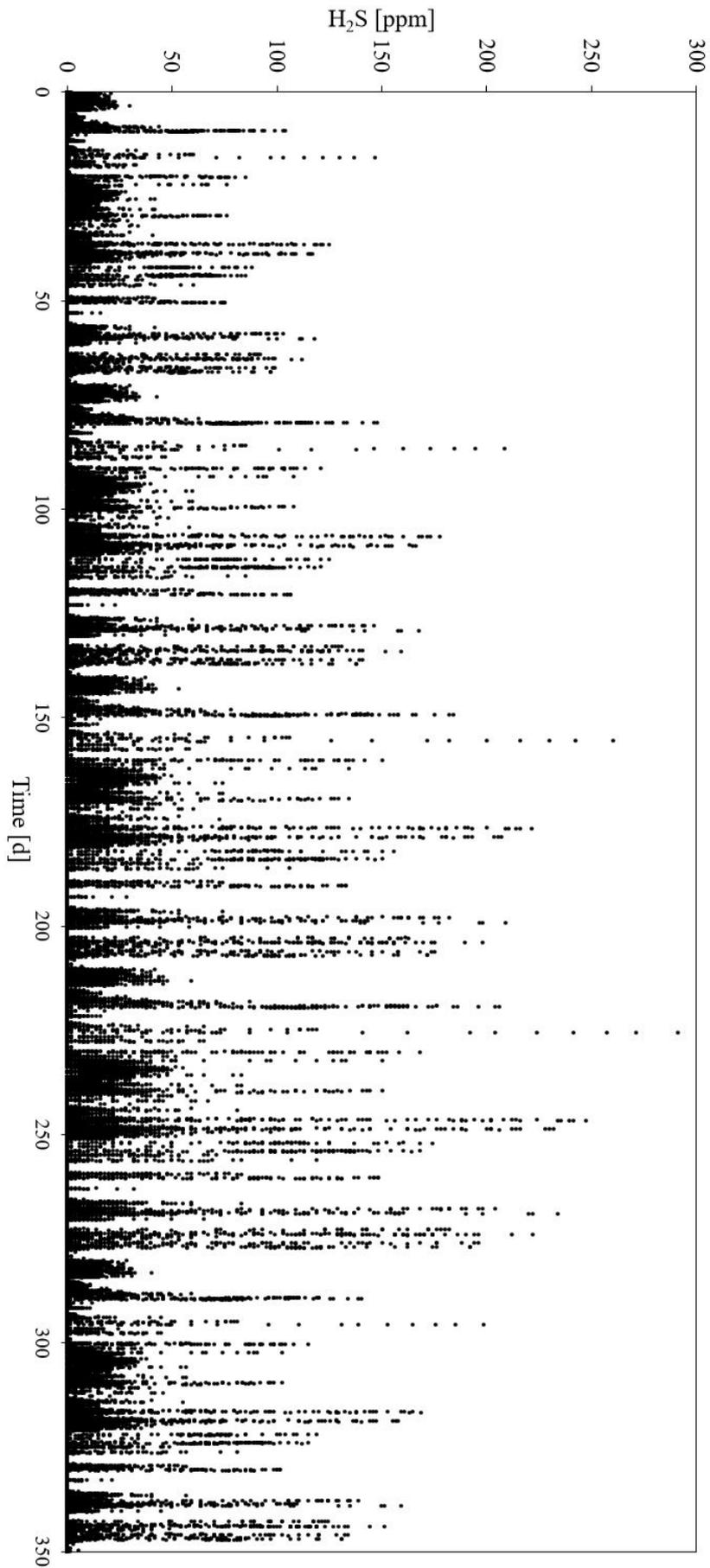


Figure 3: Concentration of H<sub>2</sub>S for 350 days where the yearly corrosion rate is calculated.

# Appendix C - Electronic Appendix

The electronic appendix contains files and documentation of the calculations in this report. The folder contains the following files:

**C1\_Carbonation\_reactor\_permeability:** Testing of the permeability of the reactor used for CO<sub>2</sub> and H<sub>2</sub>S uptake rates together with the leakage factor.

**C2\_Carbonation\_depth\_model:** Calculations for the simple carbonation penetration rates for STD<sub>C</sub> and ASC.

**C3\_ASC\_alkalinity:** Alkalinity calculation for ASC based on the experiment of Mathiasen (2019).

**C4\_CO2\_H2S\_uptake\_corrosion:** Measured and simulated uptake rates of CO<sub>2</sub> and H<sub>2</sub>S together with the corrosion rates.

**C5\_Yearly\_corrosion\_MATLAB\_code:** Algorithm used to calculate the cumulative yearly corrosion at varying concentrations of H<sub>2</sub>S from measurements near the wastewater treatment plain in Ikast.