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Identification of controlling factors for the initiation of corrosion
of fresh concrete sewers

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Abstract

The development of concrete corrosion in new sewer pipes undergoes an initiation process before reaching an active corrosion stage. This initiation period is assumed to last several months to years but the key factors affecting the process, and its duration, are not well understood. This study is therefore focused on this initial stage of the corrosion process and the effect of key environmental factors. Such knowledge is important for the effective management of corrosion in new sewers, as every year of life extension of such systems has a very high financial benefit. This long-term (4.5 year) study has been conducted in purpose-built corrosion chambers that closely simulated the sewer environment, but with control of three key environmental factors being hydrogen sulfide (H2S) gas phase concentration, relative humidity and air temperature. Fresh concrete coupons, cut from an industry-standard sewer pipe, were exposed to the corrosive conditions in the chambers, both in the gas phase and partially submerged in wastewater. A total of 36 exposure conditions were investigated to determine the controlling factors by regular retrieval of concrete coupons for detailed analysis of surface pH, sulfur compounds (elemental sulfur and sulfate) and concrete mass loss.
Corrosion initiation times were thus determined for different exposure conditions. It was found that the corrosion initiation time of both gas-phase and partially-submerged coupons was positively correlated with the gas phase $\text{H}_2\text{S}$ concentration, but only at levels of 10 ppm or below, indicating that sulfide oxidation rate rather than the $\text{H}_2\text{S}$ concentration was the limiting factor during the initiation stage. Relative humidity also played a role for the corrosion initiation of the gas-phase coupons. However, the partially-submerged coupons were not affected by humidity as these coupons were in direct contact with the sewage and hence did have sufficient moisture to enable the microbial processes to proceed. The corrosion initiation time was also shortened by higher gas temperature due to its positive impact on reaction kinetics. These findings provide real opportunities for pro-active sewer asset management with the aim to delay the on-set of the corrosion processes, and hence extend the service life of sewers, through improved prediction and optimization capacity.

**Key words**

Sewer; corrosion; hydrogen sulfide; humidity; temperature; initiation time

**Nomenclature**

- **ANOVA**: Analysis of variance
- **MAM**: Minimum adequate model
- **MIC**: Microbially induced corrosion
- **PLC**: Programmable logic controller
- **SRB**: Sulfate-reducing bacteria
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<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>44</td>
<td>SOB</td>
<td>Sulfide-oxidizing bacteria</td>
</tr>
<tr>
<td>45</td>
<td>RH</td>
<td>Relative humidity</td>
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<tr>
<td>46</td>
<td>RTD</td>
<td>Resistance temperature detector</td>
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1 Introduction

Existing sewers are valuable infrastructure and assets that have been established by continuous public investment over the period of more than the past century. These sewers have an estimated asset value of one trillion dollars in the USA (Brongers et al., 2002) and $100 billion in Australia. However, concrete corrosion is a costly deteriorating process affecting sewer systems worldwide. Corrosion causes loss of concrete mass and structural capacity, cracking of the sewer pipes and ultimately structural collapse. The rehabilitation and replacement of damaged sewers involves very high costs. The sewer assets are being lost at an estimated annual economic cost of around $14 billion in USA alone (Brongers et al., 2002) due to corrosion. This cost is expected to increase as the aging infrastructure continues to fail (Sydney et al., 1996; US EPA, 1991).

Population growth and urbanization have led to continuous expansion of existing sewers and replacement of outdated sewers. Fresh concrete sewer pipes and structures are installed worldwide due to many advantages including low costs and flexibility. However, knowledge about the development of corrosion on new concrete surfaces under sewer conditions is limited. Gravity sewers offer favorable conditions for microbially induced corrosion, such as available water (due to elevated relative humidity (RH)), high concentrations of carbon dioxide, and high concentrations of H$_2$S (Wei et al., 2014). However, the fresh concrete surface after construction is not suitable for microbial growth because of the high alkalinity. Therefore, an initiation period is required to make the surface amenable for sulfide oxidizing microorganisms.

The development of corrosion on concrete sewers can be divided into three stages, as shown in Figure 1. During stage 1, the concrete surface is changed to a more favorable environment for microorganisms due to carbonation and H$_2$S acidification (Islander et al., 1991; Joseph et
al., 2012). On the new concrete surface, owing to the presence of catalytic oxides, hydrogen sulfide is chemically oxidized to sulfur in the form of very small crystals (Bagreev and Bandosz, 2004; Bagreev and Bandosz, 2005). Overall, an important step is the dissociation of hydrogen sulfide to \( \text{HS}^- \) in the adsorbed film of water on the concrete surface. This dissociation is enhanced by the alkaline surface pH, which is an important factor for the uptake of gaseous hydrogen sulfide during this first stage (Nielsen et al., 2006b). Additionally, the chemical sulfide oxidation rate in the sewer is seen to double for a temperature increase of 9 °C by the same study. Therefore, relative humidity, \( \text{H}_2\text{S} \) concentration and temperature all play a certain role in stage 1 of the corrosion development.

(Figure 1)

During stages 2 and 3, biological sulfide oxidation by netruophilic and acidiophilic sulfide oxidising-bacteria will contribute to the sulfide oxidation to produce sulfuric acid (Cayford et al., 2012; Okabe et al., 2007). This reacts with the cement material leading to the formation of two important corrosion products: gypsum (\( \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \)) in the matrix of the corrosion layer and ettringite (\( ((\text{CaO})_3 \cdot \text{Al}_2\text{O}_3 \cdot (\text{CaSO}_4)_3 \cdot 32\text{H}_2\text{O}) \)) near the corrosion front where there is higher pH (Jiang et al., 2014b; O'Connell et al., 2010). Recent studies show that the biological sulfide oxidation rates correlate with \( \text{H}_2\text{S} \) concentration, relative humidity and temperature (Jiang et al., 2014a; Nielsen et al., 2006a; Nielsen et al., 2005).

The total time span starting from fresh concrete surface to observed mass loss of concrete is defined as the initiation time, i.e. \( t_{\text{in}} \). It is clear that the length of initiation time depends on many different factors due to the many processes and reactions involved. For a specific sewer environment, it is beneficial to estimate \( t_{\text{in}} \) for the purpose of evaluating or optimizing current corrosion prevention strategies. Although the well-known Pomeroy model can be used to calculate the deterioration rate of concrete sewer pipes (Pomeroy, 1990), no model exists for
the estimation of $t_{in}$ which is mainly due to the limited understanding of the controlling factors for the corrosion initiation. Therefore, a full understanding of the relationship between $t_{in}$ and sewer environmental factors including H$_2$S concentration, relative humidity and temperature is critical for the overall prediction of sewer corrosion.

This study aims to enhance understanding of the correlation between the initial development of sewer corrosion and the sewer environmental factors including H$_2$S concentration, relative humidity and temperature. In particular, to determine the controlling factors important for the corrosion initiation time $t_{in}$. Fresh concrete coupons, either located in the gas-phase or partially submerged in domestic wastewater, were exposed to thirty-six independent conditions in well-controlled laboratory chambers that simulated conditions typically found in various sewers, with six levels of H$_2$S concentration, two levels of relative humidity (RH) and three levels of temperature. During the extended exposure experiment (over 4.5 years), the change of surface properties, the formation of corrosion products and the mass losses due to corrosion were measured regularly. The observed results were then statistically analyzed to identify the controlling factors for the corrosion initiation time.

2 Material and Methods

2.1 Concrete coupons

The fresh concrete coupons were prepared from a new sewer pipe (1.2 m diameter × 2.4 m length and 0.07 m thickness) obtained from a sewer pipe manufacturer (HUMES, Sydney, Australia). The HUMES concrete composition includes 10-20% Portland cement, about 60% aggregates containing crystalline silica (quartz) sand, crushed stone and gravel, water at <20% and other supplementary cementitious materials. Coupon dimensions were approximately 100 mm (length) × 70 mm (width) × 70 mm (thickness). After cutting, the coupons were washed
in fresh water to remove any surface contamination. Washed coupons were then dried in an oven (Thermotec 2000, Contherm) at 60 °C for 3 days to achieve similar and stable initial water content.

(Figure 2)

One of the original surfaces of the coupons, i.e. the internal surface of the pipe, was designated as the surface to be exposed to H\textsubscript{2}S. After cutting, the coupons were mounted in stainless steel frames using epoxy (FGI R180 epoxy & H180 hardener) with the steel frame providing a reference point for determining the change in thickness due to corrosion (Jiang et al., 2014b). As described in section 2.2, the frame-enclosed coupons were used in the gas-phase exposure. In addition, the same number of concrete coupons without enclosures were partially submerged in real sewage in the corrosion chambers (Figure 3).

2.2 Corrosion chamber and exposure condition

Thirty-six identical corrosion chambers were constructed to achieve a controlled environment simulating that of real sewers (Table 1). The controlled factors include combinations of three gas-phase temperatures (17 °C, 25 °C and 30 °C), two levels of RH (100% and 90%) and six H\textsubscript{2}S levels (0 ppm, 5 ppm, 10 ppm, 15 ppm, 25 ppm and 50 ppm). The RH is sensitive to temperature and the low RH (90%) fluctuated between 85% and 95%. Temperature and H\textsubscript{2}S variations are within 1 °C and 2 ppm, respectively.

(Table 1)

The chambers were constructed of glass panels of 4 mm thickness. The dimensions of the chambers were 550 mm (L) × 450 mm (D) × 250 mm (H) (Figure 3). Each chamber contained 2.5 L of domestic sewage that was collected from a local sewer pumping station and replaced every two weeks. Seven coupons enclosed in frames were exposed to the gas
phase within the chambers with the exposed surface facing downwards approximately 110 mm above the sewage surface (Figure 3). This coupon arrangement simulated the sewer pipe crown, a location which is reported to be highly susceptible to sulfide induced corrosion (Mori et al., 1992; Vollertsen et al., 2008). Another six unmounted coupons were placed at the bottom of the chambers. These were thus partially submerged (approx. 20-30 mm) in the wastewater simulating the concrete sewer pipe near the water level, which is also a region of high corrosion activity.

(Figure 3)

To achieve the specified \( \text{H}_2\text{S} \) gaseous concentrations in the corrosion chamber, \( \text{Na}_2\text{S} \) solution was injected into a container partially filled with acid (13% HCl), using a corrosion-resistant solenoid pump (Bio-chem Fluidics, model: 120SP2440-4TV) with a dispense volume of 40 \( \mu \text{L} \). The \( \text{H}_2\text{S} \) concentrations were monitored using a \( \text{H}_2\text{S} \) gas detector (OdaLog Type 2) with a range between 0 and 200 ppm (App-Tek International Pty Ltd, Brendale, Australia). A PLC was employed to monitor the \( \text{H}_2\text{S} \) concentration and to trigger the dosing pump for \( \text{Na}_2\text{S} \) addition to maintain the specified \( \text{H}_2\text{S} \) concentrations (Figure 3).

The corrosion chambers were installed in three cabinets, i.e. A, B and C (12 chambers each cabinet), with different sewage temperatures controlled by re-circulating temperature controlled water through glass tubes immersed in the sewage. The relative humidity was thus controlled at approximately 100% or 90% for different chambers (Table 1). Humidity was monitored using two resistance temperature detector (RTD) probes, of which one acts as wet and another acts as dry bulb inside the chamber. Another of these probes was employed to monitor the sewage temperature.

2.3 Corrosion sampling and chemical analysis
The corrosion chambers were operated for 54 months since December 2009. The environmental factors were checked regularly to ensure the chambers being operated under proper conditions. Periodically, at intervals between 6-10 months, one set of coupons (one gas-phase coupon and one partially-submerged coupon) were retrieved from each corrosion chamber for detailed analysis. A standard step-by-step procedure of various analysis was employed to measure surface pH, followed by sampling for sulfur species (primarily elemental sulfur and sulfate, as other sulfur compounds were found to be at nonsignificant levels), and then photogrammetry analysis (thickness change).

A flat surface pH electrode (Extech PH150-C concrete pH kit, Extech Instruments, USA) was used to measure the coupon surface pH. Steady pH readings were obtained after sufficient contact between the pH probe and the coupon surface measuring spots that were wetted with about 1 mL of milliQ water. Four measurements were made on randomly selected spots on the coupon surface to determine an average value.

After measuring the surface pH, the exposed surface of concrete coupons was washed using a high pressure washer (Karcher K 5.20 M). Four liter of water was used for each coupon. The wash-off water was homogenized using a magnetic mixer for 2 hours before subsamples taken into sulfide anti-oxidant buffer solution. A Dionex ICS-2000 IC with an AD25 absorbance (230 nm) and a DS6 heated conductivity detector (35 °C) was used to measure the soluble sulfur species.

Five photos for each coupon were taken at different orientations to measure the coupon thickness after washing using photogrammetry. A 3D image of the exposed surface for each coupon was generated to calculate the surface height of the coupon relative to the stainless steel frame as the reference plane. The decrease in thickness after certain exposure time was then calculated by subtracting the average thickness after washing from the average thickness.
before exposure. This technique not only enables an accurate change in coupon thickness to be determined irrespective of the surface roughness but also provides a detailed record of the spatial distribution of the losses that occurred.

2.4 Data analysis

As discussed, the concrete corrosion develops in three stages where in the third stage sulfuric acid production occurs (Figure 1). Thus, we may define the corrosion initiation time, $t_{in}$, as the time taken before detection of significant levels of sulfate on the concrete surface. Taking into consideration the location of coupons and their actual sulfide oxidation rates, we determined the critical levels of sulfate arbitrarily as 1 gS/m$^2$ and 10 gS/m$^2$ for the gas-phase and partially-submerged concrete coupons respectively. Corrosion initiation time for all coupons were then calculated as the time to reach the critical levels assuming a linear increase of sulfate production with time. The estimated $t_{in}$ was subsequently analyzed to identify the controlling environmental factors of the corrosion initiation processes.

First, regression tree models (R ver 3.1.1, http://www.R-project.org/) were used to determine which of the three environmental factors were important (exploratory analysis). Tree models were used as they can give a clear picture of the structure in the data and they automatically accommodate complex interactions between explanatory variables. Recursive partitioning, that successively splits the data by the explanatory variables (i.e. H$_2$S concentration, relative humidity and gas temperature), was used to distinguish groupings in the corrosion initiation time. To further investigate the importance of each environmental factor for the corrosion initiation, statistic models with all three factors were analyzed using analysis of variance (ANOVA) in R. These maximal models were then simplified by backward selection to get minimal adequate models (MAM).

3 Results and Discussion
3.1 Surface pH

For fresh coupons exposed to 0 ppm H$_2$S for 54 months there was little change in the surface pH from an initial level of 10.6 (Figure 4). The only factor driving pH down on gas-phase coupons exposed to 0 ppm of H$_2$S would be from CO$_2$, however, this could not cause further decrease of the surface pH as the coupon surfaces had already reached an equilibrium with regard to carbonation. Extended exposure in the H$_2$S free air at different temperatures and humidity levels did not lower the pH significantly. Surface pH of partially-submerged coupons exposed to 0 ppm of H$_2$S decreased slightly, within 1 unit, after 54 months of exposure (Figure 4). This slight change could be attributed to the neutralization from CO$_2$ in the gas, and other organic acids present in the wastewater.

Reduction of surface pH on other gas-phase coupons exposed to various H$_2$S concentrations (5-50 ppm) was more significant due to the acidification by H$_2$S itself or its oxidation product, i.e. sulfuric acid (Figure. SI-2). A trend of gradual decrease in surface pH with the time of exposure is evident for gas-phase coupons exposed to H$_2$S. In general, higher H$_2$S concentrations coincided with lower surface pH. The pH drop in the 100% RH chambers was slightly more than that in 90% RH chambers. Likely, high humidity levels facilitated sulfide oxidation, as pore water is essential for chemical reactions to occur in concrete and for the development of the sulfide oxidizing microbial activities. In contrast to RH, there is no discernable effects of temperature on the coupon surface pH drop.

For partially-submerged coupons the surface pH had lowered to about 4 for 5 ppm H$_2$S, with some variations, after 54 months of exposure. The pH for coupons exposed to 10, 15, and 25 ppm H$_2$S was between 2 and 4 in the majority of the coupons. The partially submerged coupons exposed to 50 ppm H$_2$S, had their surface pH reduced to around 2 for both the 100%
and 90% RH after 34 months of exposure. No discernable effects of RH and temperature were observed on the coupon surface pH over time. Partially-submerged coupons were in close proximity to water, and were consequently less sensitive to RH levels.

In comparison to gas-phase coupons, it is evident that the decrease of surface pH is more prominent on partially-submerged coupons for all H₂S gas levels. This is partially due to the different factors contributing to the overall pH reduction. At the initial stages, the surface pH was lowered by H₂S and CO₂, which was facilitated by high moisture levels. This acidification, as evident by high sulfide oxidation activities, started earlier on the partially submerged coupons (Fig. SI-1 & SI-2).

Over time, the dominating trend was of acidification of the coupon surface. However, it was noticed in a few cases after becoming acidic, the surface pH then increased somewhat. A possible explanation for this is by oxidation of Ca(HS)₂, to form Ca(OH)₂, i.e. alkalinity, and elemental sulfur. Another possibility is that during chamber maintenance and coupon retrieval, the H₂S exposure was temporarily interrupted and alkalinity permeating from the concrete causes this slight rise in surface pH.

### 3.2 Sulfate and elemental sulfur

Levels of elemental sulfur and sulfate on coupon surfaces clearly increased with the exposure time and gaseous H₂S levels (Fig. SI-1 & SI-2). Both elemental sulfur and sulfate detected on gas-phase coupons were limited, i.e. less than 40 gS/m². The difference of elemental sulfur production on gas-phase coupons between the two RH conditions and three temperatures was not clear. Although high levels of elemental sulfur, up to 40 gS/m² were detected, this was about 10 times lower than the sulfate detected on the partially-submerged coupons (Fig. SI-2). It is evident that the surface sulfate increases with increased gaseous H₂S levels and with increased time of exposure. In the latest sampling events there were significantly higher
sulfate levels, implying very active sulfide oxidation, likely this resulting from the biological processes being more active. No discernible differences were found for sulfate concentrations between the two RH levels. For the partially submerged coupons at least, these would have an increased moisture content as water would be drawn up from the submerged surface to the corrosion layer, and thus overriding the effect of RH differences.

The first peak shown in the profiles of elemental sulfur without sulfate being present suggests that the neutrophilic sulfide oxidizing microbes produce mainly elemental sulfur at the corresponding intermediate pH levels. With the following decrease of surface pH, the accumulated elemental sulfur was further oxidized to sulfate, probably by another group of sulfide oxidizing microbes. At low pH, some elemental sulfur was detected on the coupon surface (Figure SI-1). Likely this is due to elemental sulfur being a temporary intermediate of sulfide oxidation, which is then finally oxidized to sulfate. The formation of elemental sulfur is attributed to both chemical and biological sulfide oxidation (Okabe et al., 2007). It has also been observed that S\(^0\) can be temporarily stored in the corroding concrete layer when high gaseous H\(_2\)S levels occur (Jensen et al., 2009; Sun et al., 2014).

As the concrete mass loss occurs by reactions with sulfuric acid, the percentage of sulfate indicates the progress of the development of corrosion. Figure 5 shows evidently increasing trend of sulfate percentage with exposure time, which is in accordance with the succession of sulfide oxidizing microorganisms (Figure 1). Partially-submerged coupons achieved 100% of sulfide oxidation to sulfate for both 100% and 90% RH levels after 24 months of exposure. However, the sulfate percentage on gas-phase coupons increased steadily with exposure time, with higher levels attained for coupons exposed to 100% RH in comparison to 90% RH.

(Figure 5)
It was seen that the sulfate produced on gas-phase coupons at 90% RH was still lower than the elemental sulfur, with the percentage as sulfate was most often less than 50% (Figure 5). It is reported that for H$_2$S gas concentrations of between 5 and 50 ppm there is a surface pH threshold of 8.3-9.4, that influences the extent of H$_2$S oxidation. Due to oxygen limitations in the liquid film on the coupon surface, partial oxidation only occurs above the pH threshold, and sulfate formation is only favored when the surface pH is below this threshold (Joseph et al., 2012). For each of the H$_2$S levels above 5 ppm (10, 15, 25, and 50 ppm), the gas-phase coupon surface pH has decreased to levels lower than the threshold (8.3-9.4) after nearly 3 years of exposure. The attenuating surface pH on those coupons would have led to the complete oxidation of H$_2$S to form sulfate. Collectively, these observations confirmed that gas-phase coupons are still in the early stage of corrosion: where a significant part of acidification would mainly occur by H$_2$S.

Both gypsum (CaSO$_4$) and ettringite (Ca$_6$Al$_2$(SO$_4$)$_3$(OH)$_{12}$·26H$_2$O) can be formed in the corrosion layer due to the production of sulfuric acid. Measured molar ratios between calcium and sulfur (Ca:S) on the coupons were around 1.4 (0.8 – 2.5), which indicates the corrosion products contain both gypsum and ettringite that have Ca:S molar ratios of 1 and 2 respectively. The high surface pH of the gas-phase coupons also favors the conversion of gypsum into ettringite (Jiang et al., 2014b).

### 3.3 Corrosion losses

The thickness of gas-phase concrete coupons only started to decrease due to corrosion loss after 34 months of exposure (Figure 6), reaching a maximum at the end of the exposure period of 2-3 mm for high H$_2$S levels (25 and 50 ppm). These gas-phase coupons had a low corrosion rate in this initial period. It is not evident that concrete coupons exposed to 100% RH induced more corrosion losses than those under 90% RH, although higher sulfate was
detected for high RH coupons (Fig. SI-2). It is highly possible that higher levels of moisture promote more active biological and or chemical sulfide oxidation, to produce higher concentrations of sulfuric acid or elemental sulfur. However, the noticeable low levels of sulfate detected on gas-phase coupons, in comparison to that on the partially-submerged coupons, indicates that the corrosion is limited by the sulfide-oxidizing rate rather than H$_2$S concentration. (Figure 6)

In contrast, the corrosion loss of the partially-submerged concrete coupons had reached more than 4 mm for those exposed to 25 and 50 ppm H$_2$S (Figure 6). This corresponds well to the high measured sulfate levels on these coupons (Fig. SI-2). It is clear that corrosion losses are directly correlated to H$_2$S concentrations (Figure 6). This suggests that H$_2$S is the decisive factor for the corrosion rate, as reported before on pre-corroded concrete sewer (Jiang et al., 2014a). This is in contrast to the gas-phase coupons, where it is likely that microbial activity is the determining factor and hydrogen sulfide was not a limiting factor in this early stage of corrosion initiation. Partially-submerged coupons are continuously inoculated and wetted with wastewater in the corrosion chambers. Consequently, sulfide-oxidizing microbes might be better developed on these coupons in comparison to the gas-phase coupons.

### 3.4 Corrosion initiation time

Corrosion initiation time, $t_{in}$, was determined for both gas-phase and partially-submerged concrete coupons (Figure 7). For the gas-phase coupons $t_{in}$ was more or less similar at 20 months for the different H$_2$S concentrations, except that of 5 ppm H$_2$S ($p=0.0079$, Table 2). The expected trend of decreasing corrosion initiation time with increasing H$_2$S levels was not evident. Instead, H$_2$S above 5 ppm seems to be a critical point for the $t_{in}$, implicating a certain level of H$_2$S is required for significant corrosion development. This supports our findings of
corrosion losses on gas-phase coupons, which indicates corrosion is limited by the sulfide oxidation rate, not the H$_2$S concentration (Section 3.3). For these gas-phase coupons it is evident also that $t_{in}$ decreases with higher temperature and higher humidity (Figure 7). Both the Tree (Figure SI-3) and the ANOVA analyses (Table 2) were consistent with these findings, emphasizing the importance of temperature and relative humidity on $t_{in}$, with ANOVA $p$ values of $5.95 \times 10^{-6}$ and $6.86 \times 10^{-7}$ for relative humidity and gas temperature, respectively. (Figure 7)

It is noticeable that for partially-submerged coupons the corrosion initiation time decreases with increased H$_2$S concentration ($p=0.0044$). This confirms that H$_2$S is a key controlling factor of the $t_{in}$ over periods of long term exposure in sewer conditions. Temperature was again shown to be a significant factor affecting the corrosion initiation time, with a $p$ value of 0.0063. As found for the coupon surface sulfur compounds and corrosion losses (Section 3.2 and 3.3), the humidity was not a significant factor for $t_{in}$ ($p=0.7459$). The data in Fig. 7 also suggest that corrosion likely starts with the water line and reaches the crown gradually as reported previously (Vollertsen et al., 2008). A minimum adequate model (MAM) was thus identified through the backward selection processes which drops one explanatory factor for the $t_{in}$ each time. The MAM for gas-phase coupons includes all three experimental factors, while the MAM for partially-submerged coupons only requires H$_2$S concentration and temperature (Table 2).

(Table 2)

### 3.5 Practical implications

The observations of this study identified the controlling environmental parameters for the initiation of corrosion on sewer concrete. The findings are relevant to develop strategies for
the prevention or reduction of sewer corrosion by prolonging the initiation time. One obvious
solution would be to reduce gaseous \( \text{H}_2\text{S} \) concentration, which could be achieved by dosing
sulfide sequestering agents or sewer biofilm controlling agents (Ganigue et al., 2011; Jiang et
al., 2013; Jiang et al., 2015; Jiang and Yuan, 2013; US EPA, 1974). However, it should be
noted that unless gaseous \( \text{H}_2\text{S} \) concentrations can be reduced down to below 5 ppm, the
corrosion initiation would still progress at the same pace for sewer crown areas (similar to the
gas-phase coupons in the corrosion chamber). It should also be noted that the corrosion
initiation time was only reduced from around 25 months at 50 ppm to 15 months at 5 ppm
(Figure 7), i.e. a 40% reduction of corrosion initiation time for a 90% reduction of \( \text{H}_2\text{S} \)
concentration. Also, liquid-phase technologies are not capable of reducing the relative
humidity in a sewer system. In contrast, sewer ventilation and gas treatment could be used to
decrease both \( \text{H}_2\text{S} \) and humidity, and consequently these would be more effective strategies
for prolonging the initiation of corrosion.

Another type of technology for preventing corrosion is by pipe relining or coating with
plastic or epoxy resins (Hewayde et al., 2007; Valix et al., 2012). These materials are more or
less inert to sulfuric acid. However, the coating material usually doesn’t have alkaline
buffering capacity as fresh concrete, which means the surface can be easily inhabited by
acidiophilic sulfide-oxidizing bacteria due to the quick drop of surface pH. Consequently,
high concentrations of sulfuric acid will form on the sewer coating surface, which
inevitability will reduce the performance and life time of the coating. Other products might
provide such a sacrificial material like magnesium hydroxide, which will be eventually
exhausted but can slow down the corrosion development. It should be noted that the
corrosion initiation was largely due to the biological activity of sulfide oxidizing bacteria
enhancing sulfuric acid production. Pipe coating or relining materials that provide
antimicrobial properties and inhibit the microbial development on coating surfaces might be
the most useful strategies to ameliorate the damaging effects (Haile et al., 2010; Hashimoto, 2001). However, all corrosion reduction practice will lead to higher gaseous H$_2$S concentration, potentially causes more odor problems.

4 Conclusions

The initiation of corrosion on fresh concrete surfaces in sewers was investigated in a 4.5-year exposure study, which demonstrated that three elements were mainly affecting this process:

- Gas-phase H$_2$S concentration is an essential factor in initiating concrete corrosion under sewer conditions. However, the corrosion is only limited by the H$_2$S supply at concentrations at or below 10 ppm. At higher H$_2$S concentrations the sulfide oxidation rate was the limiting factor during the initiation stage. This is contrary to the long-term sulfide corrosion processes where even higher H$_2$S concentrations were still increasing the corrosion rates.

- The corrosion initiation was positively correlated with the gas-phase temperature mainly due to chemical reactions involved. This suggests a more rapid onset and higher occurrence of sewer corrosion in warmer climates, and may be further enhanced by ongoing climatic changes and increasing temperatures in urban areas.

- For concrete surfaces exposed to sewer air, humidity plays a significant role to provide moisture to the concrete surface via vapor condensation. Moisture is important for both the initiation and active corrosion stages. Ventilation can thus delay the on-set and possibly mitigate against sewer corrosion through reduced humidity.

Acknowledgements
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References


Table 1. Controlled environmental factors for the 36 corrosion chambers.

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B [25 °C]   |        |            |        |            |        |            |
C [30 °C]   |        |            |        |            |        |            |
Table 2. Analysis of variance (ANOVA) for the corrosion initiation time ($t_{in}$) of gas-phase concrete coupons.

<table>
<thead>
<tr>
<th>Factors</th>
<th>$t_{in} \sim H_2S + RH + T$ (Minimum adequate model)</th>
<th>$t_{in} \sim H_2S + RH + T$</th>
<th>$t_{in} \sim H_2S + T$ (Minimum adequate model)</th>
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<tbody>
<tr>
<td></td>
<td>Df</td>
<td>Sum of Sq</td>
<td>RSS</td>
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<td>T</td>
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1 Df stands for degree of freedom; RSS, residual sum of square; Pr(>F), the p-value using the F-test.
2 Significance codes based on the Pr value: 0.001-0.0001: ***; 0.001-0.01: **; 0.01-0.05: *; 0.05-0.1: .; 0.1-1: NA.
Figure 1. The development of microbially induced corrosion on new concrete sewer surfaces, adapted from Islander et al. (1991), with the corrosion initiation time ($t_i$) including stage 1, 2 and a part of stage 3.

Figure 2. Photos of (A) a fresh concrete coupon; (B) the coupon mounted on a stainless steel frame with epoxy.
Figure 3. Side view of the corrosion chamber with H$_2$S concentration, relative humidity and gas temperature controlled by programmable logic controller (PLC).
Figure 4. Surface pH of fresh concrete coupons exposed to different H$_2$S concentrations in corrosion chambers for 54 months. Plots in columns 1 & 2 and columns 3 & 4 are for coupons located in the gas-phase and those partially-submerged in sewage, respectively. Filled and empty symbols are for 100% and 90% relative humidity respectively.
Figure 5. Percentage of sulfate as the final product of sulfide oxidation on the surface of fresh concrete coupons exposed to different H$_2$S concentrations in corrosion chambers for 54 months. Plots in columns 1 & 2 and columns 3 & 4 are for coupons located in the gas-phase and those partially-submerged in sewage, respectively. Filled and empty symbols are for 100% and 90% relative humidity respectively.
Figure 6. Corrosion losses of fresh concrete coupons exposed to different H₂S concentrations in corrosion chambers for 54 months. Plots in columns 1 & 2 and columns 3 & 4 are for coupons located in the gas-phase and those partially-submerged in sewage respectively. Filled and empty symbols are for 100% and 90% relative humidity respectively.
Figure 7. Box-plots of corrosion initiation time of concrete coupons related to H$_2$S concentration, relative humidity and gas temperature in the corrosion chambers. Plots in the upper row are for coupons located in the gas-phase and those in the lower row are for the partially submerged coupons.
**Highlights**

- A long-term study (4.5 years) focusing on the initiation of $\text{H}_2\text{S}$ induced sewer corrosion
- The sulfide oxidation products gradually transform from elemental sulfur to sulfuric acid
- Corrosion initiation is controlled by $\text{H}_2\text{S}$ only when the level is at or below 10 ppm
- Corrosion initiation is highly correlated with the gas temperature
- Humidity is important for the corrosion initiation on concrete exposed to air
Supplementary Information

Title: Identification of controlling factors for the corrosion initiation on concrete sewers

Authors: Guangming Jiang, Xiaoyan Sun, Jurg Keller, Philip L. Bond

Tables: 0

Graphs: 3
Figure SI-1. Elemental sulfur measured on the surface of fresh concrete coupons exposed to different H2S levels in the corrosion chambers for 54 months. Plots in columns 1 & 2 and columns 3 & 4 are for coupons located in the gas-phase and those partially-submerged in sewage, respectively. Filled and empty symbols are for 100% and 90% relative humidity respectively.
Figure SI-2. Sulfate measured on the surface of fresh concrete coupons exposed to different H2S levels in the corrosion chambers for 54 months. Plots in columns 1 & 2 and columns 3 & 4 are for coupons located in the gas-phase and those partially-submerged in sewage, respectively. Filled and empty symbols are for 100% and 90% relative humidity respectively.
**Figure SI-3.** Trees for the corrosion initiation time of concrete coupons located in the gas-phase and those partially submerged in wastewater (from left to right). The expressions at each branch node are the splitting factor and the levels. E.g. $\text{H}_2\text{S} < 12.5$ means the corrosion rates can be partitioned into two groups by different $\text{H}_2\text{S}$ levels. The left branch is the data for $\text{H}_2\text{S} < 12.5$ ppm and the right is for $\text{H}_2\text{S} \geq 12.5$ ppm. The numbers at the end of each branch are the mean values for the corrosion initiation time in that group. The analysis shows that different experimental factors contribute to the difference in the corrosion initiation time.