The rapid chemically induced corrosion of concrete sewers at high H2S concentration

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Keywords
h2s concentration, induced, corrosion, concrete, rapid, sewers, chemically, high

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The Rapid Chemically Induced Corrosion of Concrete Sewers at High H$_2$S Concentration

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Highlights:

- The first report of chemically induced concrete corrosion in sewers
- High concentration of H$_2$S can be chemically oxidized into sulfuric acid at sewer crown
- Sulfide oxidizing microorganisms were not participating in the rapid corrosion
Abstract:
Concrete corrosion in sewers is primarily caused by H₂S in sewer atmosphere. H₂S concentration can vary from several ppm to hundreds of ppm in real sewers. Our understanding of sewer corrosion has increased dramatically in recent years, however, there is limited knowledge of the concrete corrosion at high H₂S levels. This study examined the corrosion development in sewers with high H₂S concentrations. Fresh concrete coupons, manufactured according to sewer pipe standards, were exposed to corrosive conditions in a pilot-scale gravity sewer system with gaseous H₂S at 1100±100 ppm. The corrosion process was continuously monitored by measuring the surface pH, corrosion product composition, corrosion loss and the microbial community. The surface pH of concrete was reduced from 10.5 ± 0.3 to 3.1 ± 0.5 within 20 days and this coincided with a rapid corrosion rate of 3.5 ± 0.3 mm year⁻¹. Microbial community analysis based on 16S rRNA gene sequencing indicated the absence of sulfide-oxidizing microorganisms in the corrosion layer. The chemical analysis of corrosion products supported the reaction of cement with sulfuric acid formed by the chemical oxidation of H₂S. The rapid corrosion of concrete in the gravity pipe was confirmed to be caused by the chemical oxidation of hydrogen sulfide at high concentrations. This is in contrast to the conventional knowledge that is focused on microbially induced corrosion. This first-ever systematic investigation shows that chemically induced oxidation of H₂S leads to the rapid corrosion of new concrete sewers within a few weeks. These findings contribute novel understanding of in-sewer corrosion processes and hold profound implications for sewer operation and corrosion management.

Key words: Sewer, Corrosion, Concrete, Hydrogen sulfide, Chemically Induced Corrosion
1. **Introduction**

As one of the most critical components of the urban infrastructure in modern societies, sewer networks collect and transport sewage to treatment plants, preventing human exposure to unhygienic sewage and related sewage-borne diseases. The prevalence of concrete corrosion weakens the structural strength of sewers and leads to early collapse of pipes (Zhang et al. 2008). The damage inflicted on many sewer networks and the cost of preventive measures is a significant world-wide economic problem (Alexander et al. 2013, Jiang et al. 2015a). In addition to enormous sewer remediation expenditure, the structural failure also poses potential issues of odor emission and public safety (Jiang et al. 2017).

The corrosion of concrete pipes is mainly a result of hydrogen sulfide (H$_2$S). H$_2$S is formed by sulfate-reducing bacteria (SRB) in the anaerobic sewer biofilms/sediments. From the sewage, H$_2$S is emitted to the sewer air, part of which is absorbed/adsorbed into the moisture layer on the concrete walls exposed to air, here it is oxidized to sulfuric acid and causes corrosion (Li et al. 2017). H$_2$S is ubiquitous in sewer systems, although the concentrations differ temporally and spatially from a few ppm to several hundred ppm (Jiang et al. 2014, Wells and Melchers 2015).

Sewer concrete corrosion is a relatively slow process that may take years or decades to occur (Joseph et al. 2012). A three-stage concept proposed by Islander et al. (1991) is widely adopted to describe the corrosion development. In the initiation stage, the surface pH of the concrete is reduced from c.a.13 to c.a. 9 by carbonation and H$_2$S dissolution. This leads to the later stages where the pH of the concrete surface is conducive for microorganisms to colonize. Depending on the pH, both neutrophilic and acidophilic sulfide oxidizing microorganisms will biologically oxidize sulfur compounds to sulfuric acid. The reaction between cementitious material and sulfuric acid produces corrosion products like gypsum (CaSO$_4$), resulting in the structural
weakening of concrete sewers (Davis et al. 1998, Harrison Jr 1984, Islander et al. 1991, Nica et al. 2000, Parker 1947). Since the biological oxidation rate is much higher than the chemical oxidation rate, microbial induced sulfuric acid production is regarded as the main cause for the sewer concrete corrosion (Hvitved-Jacobsen et al. 2013).

Current strategies for controlling sewer corrosion are targeted to: (1) prevent \( \text{H}_2\text{S} \) production and its partition from the sewer liquid phase through the dosing of antimicrobials, iron salts, pH elevating compounds and oxidants to the sewage; (2) reduce the \( \text{H}_2\text{S} \) concentration in sewer air through forced ventilation; (3) applying surface treatment on concrete sewers (Jiang et al. 2015a). Corrosion resistant materials like antimicrobials, silver-loaded zeolite, and polymers coatings are widely used to mitigate the corrosion of sewers (Berndt 2011, De Muynck et al. 2009, Haile and Nakhla 2010, Sun et al. 2015).

With the increased use of corrosion-resistant materials and surface treatments in sewers, instead of reacting with concrete, the \( \text{H}_2\text{S} \) in sewer air can accumulate to very high concentrations. In real sewers, \( \text{H}_2\text{S} \) concentrations of over 800 ppm are observed in a gravity pipe (Wells and Melchers 2015). Furthermore, various factors such as high wastewater sulfate concentrations, and extended hydraulic retention times can lead to high sewer \( \text{H}_2\text{S} \) concentrations (Lahav et al. 2004, Sharma et al. 2008).

To date, microbially induced sulfuric acid generation from \( \text{H}_2\text{S} \) is considered as the major contributing cause of sewer mass loss and structure failure. However, elevated \( \text{H}_2\text{S} \) concentrations in sewers might result in changed corrosion mechanisms and processes. In particular, the chemical oxidation rate of sulfide would be greatly increased, due to the reaction’s \( n \)th order kinetics \( (n = 0.90–1.38) \) (Chen and Morris 1972, Haaning Nielsen et al. 2004). Considering the relative slow growth of sulfide oxidizing microorganisms and the potential toxicity of \( \text{H}_2\text{S} \), the chemical oxidation could play a more important role than the microbial oxidation to the corrosion under high sewer \( \text{H}_2\text{S} \) conditions.
The kinetics of the chemical oxidation of \( \text{H}_2\text{S} \) on the concrete surface has received limited attention (Æsøy et al. 2002). The pathway of microbial oxidation of \( \text{H}_2\text{S} \) has been studied previously and elemental sulfur, thiosulfate, and sulfate are reported as the possible oxidation products/intermediates (Li et al. 2017, Nica et al. 2000, Parker 1945a). Very few studies have investigated the concrete corrosion induced by chemical sulfide oxidation. \( \text{H}_2\text{S} \) absorption and oxidation on corroding concrete surfaces was examined at peak concentrations around 1000 ppm (Vollertsen et al. 2008). Here they reported that the \( \text{H}_2\text{S} \) oxidation rate was as high as 1 mg S m\(^{-2}\) s\(^{-1}\) and it followed the \( n \)th order kinetics \((n = 0.45–0.75)\). However, the study did not differentiate whether the rapid sulfide oxidation was chemical or biological. Another study has investigated the abiotic and biotic oxidation of hydrogen sulfide in an acidic solution containing active concrete corrosion products {Jensen, 2009 #246}. In this study, the abiotic oxidation was much slower compared with the biotic oxidation. But the oxidation products of sulfide were not examined for abiotic oxidation and the abiotic kinetics were limited to acidic solution containing corrosion layer.

Unlike in concrete systems, numerous investigations regarding the chemical sulfide oxidation have been carried out in water, where pH shows significant impact on the oxidation process. In acidic solutions, the chemical oxidation rate is slow at pH < 6 and once the pH increases through 7 to 11, the oxidation rate increases greatly (Chen and Morris 1972). On concrete surface, the condensation water layer provides the essential medium for the chemical and biological sulfide oxidation reactions. It is thus possible that the newly manufactured concrete sewers, that will have high surface pH, are susceptible to the corrosion caused by chemical oxidation of sulfide at high \( \text{H}_2\text{S} \) concentrations.

Thus, at high \( \text{H}_2\text{S} \) concentrations, the three-stage concept of corrosion development for newly manufactured concrete sewers, it is likely very important to consider the contribution of chemical sulfide oxidation prior to the occurrence and contribution of microbially induced corrosion.
corrosion. To our knowledge, no systematic investigation has been conducted to monitor the corrosion under high H₂S concentrations and to determine the corrosion behavior, including corrosion rate and products, of newly constructed concrete sewers.

In this study, the development of corrosion was studied in detail on concrete coupons exposed in a pilot sewer system with high H₂S concentrations (1100±100 ppm). The corrosion rate, processes and products were determined by measuring the changes of concrete properties such as surface pH, sulfide oxidation products, microbial communities on the surface and mineralogy. Batch tests were then performed to determine the sulfide oxidation kinetics in the presence of fresh concrete powder or corrosion products. The knowledge obtained regarding the chemically induced corrosion of concrete has important practical implications for sewer operation, maintenance and management.

2. Materials and methods

2.1. Concrete mix design and property

Concrete coupons were prepared according to the mix design (Table 1) in compliance with the Australian standard (Standard AS2972) (2010). The cement (General Blended cement, Cement Australia Builders Cement) used nominally contains up to 25% fly ash. Four types of aggregates were used, including crushed aggregate (10 mm) with nominal maximum size of 10 mm; crushed manufactured sand (MS); natural river sand (RS) and natural fine sand (FS). For the better workability and moderate slump retention, super plasticizer (MasterGlenium SKY 8700, BASF, Australia) was also added (Table 1).

<table>
<thead>
<tr>
<th>Table 1. Concrete coupon mix design and properties</th>
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<tr>
<td>W/C(^a)</td>
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\(^a\) W/C: Water to cement ratio.
<table>
<thead>
<tr>
<th>Constituent</th>
<th>10mm</th>
<th>MS</th>
<th>RS</th>
<th>FS</th>
<th>TOTAL</th>
<th>Super plasticiser</th>
</tr>
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<tbody>
<tr>
<td>0.40</td>
<td>420</td>
<td>753</td>
<td>376</td>
<td>282</td>
<td>1882</td>
<td>4.2</td>
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<td>63</td>
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\(^a\) Constituents are given as mass needed to form 1 m\(^3\) of concrete

\(^b\) W/C: water/cement mass ratio

Properties of the concrete including compressive strength, density, shrinkage, slump and apparent volume of permeable voids were measured in accordance with the AS 1012.9 (Australian Standard 1986) for the requirements of sewer pipe (Table 1, Table S1). The acid neutralization capacity (ANC) was determined by titrating a given mass of the concrete against various quantities of 0.4 M sulfuric acid using the methods adapted from (Sun et al. 2014) and as described in section 1.2-S1.

Concrete coupons were cast with dimensions of 100 mm (length) × 70 mm (width) × 50 mm (thickness). The coupons were cured in moist air for 24 h and then cured in lime-saturated water for 28 days. After curing, the coupons were dried in an oven (Thermotec 2000, Contherm) at 60 °C for 3 days to achieve similar and stable initial water content (Joseph et al., 2010). Two dried coupons were then embedded as a pair in a stainless steel frame, providing a reference point for determining the change in thickness due to corrosion (Jiang et al., 2014). And then coupons was enclosed with one surface exposed for each coupon using epoxy (FGI R180 epoxy & H180 hardener).

2.2. Corrosion tests in the pilot-scale gravity sewer pipe

The pilot-scale gravity sewer pipe (225 mm ID PVC pipes), located in the Luggage Point Wastewater Treatment Plant (WWTP, Brisbane, Australia) (Figure 1), had a total workable length of 300 meters with an overall slope at 0.56%. Raw wastewater of the WWTP influent
was fed to the gravity pipe continuously at 100 L min\(^{-1}\). The wastewater contained dissolved sulfide at 27.2±0.5 mg-S L\(^{-1}\), sulfate at 15-20 mg-S L\(^{-1}\), and chemical oxygen demand (COD) at 550–620 mg L\(^{-1}\). The pilot sewer system was controlled by a programmable logic controller (PLC), and the operation state was manipulated using the Lab-View (Lab-View 2014, Real Time) (Song et al. 2018a).

Figure 1. Photo of the pilot-scale gravity sewer system (A) and a schematic diagram of the pipe and the coupon installment for corrosion tests (B)

Four concrete coupons, enclosed in stainless-steel frames, were installed in the gas-phase of the gravity sewer pipe, at about 250 meters away from the sewer inlet. The coupons were placed on a plastic shelf inside the pipe so that the exposed surface was facing downwards, approximately 110 mm above the sewage level (Figure 1). This coupon arrangement simulated the sewer pipe crown, a location which is reported to be highly susceptible to corrosion damage (Islander et al. 1991). A H\(_2\)S sensor (App-Tek OdaLog® Logger L2, detection range of 0-2000 ppm) was employed for the continuous monitoring of gaseous H\(_2\)S and temperature in the pipe at the coupon location. The relative humidity (RH) was measured weekly using a hand-held humidity meter (HM70, Vaisala, Australia). After 20 days of exposure the four concrete
coupons were retrieved for detailed chemical and biological analysis as described in the following sections.

2.3. Sulfide oxidation rate (SOR) of coupons

To determine sulfide oxidation rates (SOR), sulfide uptake rates (SUR) of two coupons under 500-1500 ppm H$_2$S were measured after 20 days’ exposure in the sewer pipe using the method described in Sun et al. (2014). Briefly, coupons retrieved from the pilot sewer were stored in a chamber with 100% humidity until placed into the H$_2$S uptake reactor where the relative humidity was controlled at 100%. To measure the SUR of each target concentration (i.e. $C_i$, ppm), H$_2$S gas was generated in a bottle and injected into the reactor to achieve a gaseous concentration 20 ppm higher than the target concentration (i.e. $C_i + 20$, ppm). The H$_2$S level in the reactor was then monitored continuously using a H$_2$S detector (App-Tek OdaLog® Logger L2, detection range of 0-2000 ppm). The average SUR of the coupon at each target level was calculated from 3 to 5 replicate measurements using the monitored H$_2$S profiles (Sun et al., 2014). H$_2$S uptake data of the concrete coupons were determined in the presence of either air (SUR$_{Air}$) or nitrogen gas to exclude oxidation reactions (SUR$_{Nitrogen}$). Based on these two SUR measurements, the sulfide oxidation rate (SOR) of a concrete coupon was defined as:

$$ SOR = SUR_{Air} - SUR_{Nitrogen} $$

To determine the chemical oxidation rate of sulfide, the surface of two coupons were sprayed with 50 ml 70% ethanol and then left to dry in a laminar flow sterile hood for 2 hours (Gu et al. 1998). The sterilized samples were then equilibrated with 100% humidity until a constant weight and then the SOR of the sterilized coupons was measured in the reactor as described above using a H$_2$S detector (App-Tek OdaLog® Logger L2, detection range of 0-200 ppm).

2.4. Analysis of corrosion on concrete coupons
The concrete surface pH of each coupon was determined by a flat surface pH electrode (RapidRH® potable pH kit, Wagner) (Sun et al., 2014). Four independent measurements at different locations on the same coupon were used to calculate the average value.

The corrosion products on the surface of the exposed concrete coupons were then sub-sampled for the analysis of sulfur compounds and microbial communities. For soluble sulfate measurement, samples from a known surface area (4 independent locations) of each coupon was scraped using a clean scalpel blade, dispersed into sulfide anti-oxidant buffer solution and then measured using ion chromatography (Dionex ICS-2000)(Keller-Lehmann et al. 2006). For elemental sulfur analysis, corrosion products collected from known surface area (4 independent locations) were treated to convert elemental sulfur to thiosulfate, which was then determined using ion chromatography (Dionex ICS-2000) (Jiang et al. 2009).

For DNA extraction, in order to get sufficient amount of sample, all the corrosion products, except used for sulfur compounds measurements, from four coupons were collected with a sterile surgical scalpel into a sterile 50 mL polypropylene falcon tube. The products were mixed, separated into duplicate samples and stored at 4 °C for less than 24 h. Wastewater samples were taken directly from the gravity pipe through sampling ports and stored at 4 °C for less than 24 h. The cells were separated from the corrosion products using a sucrose density gradient and DNA of the corrosion products and wastewater samples were extracted using the Fast DNA™ SPIN Kit for Soil (MP Biomedicals, CA, USA), as previously described (Jiang et al. 2016b). To perform 16S rRNA gene amplicon sequencing (Illumina), extracted DNA samples were provided to the Australia Center for Ecogenomics (ACE, Brisbane, Australia). The extracted 16S rRNA gene was amplified using the universal primer set 926F (5’-AAACTYAAAAGAATTGACGG-3’) and 1392R (5’-ACGGGCGGTGTGTRC-3’). The resulting PCR amplicons were purified using Agencourt AMPure XP beads (Beckman Coulter). Then the purified DNA was indexed using the Illumina Nextera XT 384 sample Index Kit A-
D (Illumina FC-131-1002) in standard PCR conditions with Q5 Hot Start High-Fidelity2X Master Mix. The indexed amplicons were pooled together in equimolar concentrations and sequenced on MiSeq Sequencing System (Illumina) at ACE according to manufacturer's protocol.

Raw sequencing data were quality-filtered and demultiplexed using Trimmomatic, with poor-quality sequences trimmed and removed. Subsequently, high-quality sequences at 97% similarity were clustered into operational taxonomic units (OTUs) using QIIME with default parameters, and representative OTU sequences were taxonomically BLASTed against the Greengenes 16S rRNA database. Finally, an OTU table consisting of the taxonomic classification and OTU representative sequences was produced.

To examine the chemistry and mineralogy of corrosion products formed on the concrete surface, small slices of exposed surface from each coupon (four in total) were carefully removed using a chisel, and dried in a vacuum oven (SEMSA OVEN 718) at 60 °C for 8 h. The dried samples were then coated twice by a carbon coater (Quorum Q150T, UK), following the three heavy-burst model to obtain the carbon thickness of 30-40 nm. Coated samples were analyzed by the scanning electron microscopy (SEM) (JEOL JSM-6610, America) equipped with a detector (Oxford 50mm2 X-Max SDD x-ray) that enables simultaneous imaging and elemental analysis at high count rates with 125 eV energy resolutions. The EDAX software (EDAX, AMETEK Inc) was utilized, at a frame resolution of 1024×800, with a dwell time of 200 s/frame, to collect 16 frames for each region of interest. The locations for spot analyses were not random, but chosen by examining the BSE (Backscattered electron) image, which was typically used to identify the boundaries of mineral phases (Song et al. 2018b).

After all the measurements mentioned above, the exposed surfaces of concrete coupons were washed using a high-pressure washer (Karcher K 5.20 M). The corrosion loss from the surface
of each coupon was calculated based on the point mesh generated before and after exposure, using the photogrammetry approach (Jiang et al. 2015b, Wells et al. 2009).

**2.5. Batch tests: sulfide oxidation in the presence of concrete and corrosion products**

Batch tests were performed to determine the oxidation of hydrogen sulfide by oxygen in the presence of crushed powder from fresh concrete or corrosion products based on a modified method (Jensen et al. 2011). The batch tests were conducted in a glass reactor with 800 mL working volume at 24 ± 0.5 °C (Figure S1). A pH sensor (pH 150, Oakton) and a dissolved oxygen (DO) sensor (LDO101, HQ40d, Hach) were mounted to the reactor and sealed with Teflon tape (Oxygen tape, Unasco Pty Ltd, Sydney, Australia). The solution was mixed at 100 rpm using a magnetic stirrer (Heidolph MR3000). A 50 mL syringe filled with the testing solution was used as a sample replacer to avoid headspace or negative pressure inside the reactor during sampling.

For fresh concrete powder, samples cut from the center of new concrete were disaggregated in an agate mill, then the aggregate free material was crushed to <0.5 mm particles and then mixed together with the aggregates collected from disaggregation process. Corrosion products were collected using a sterile surgical scalpel from a corroding concrete coupon, which was partially submerged in wastewater in the pilot-scale gravity pipe (Figure 1) for one month. The corrosion products were autoclaved at 120°C for 20 minutes, and then cool down to 20 °C. For each test, either crushed fresh concrete powders (20 g) or autoclaved corrosion products (10 g) were transferred into the reactor with aerated milli-Q water.

Duplicate tests were carried out with no headspace in the reactor. At the beginning of each test, the sulfide stock solution (about 300 mg-S L⁻¹) was prepared using Na₂S·9H₂O. The sulfide was added to the reactor to achieve 5.0-6.5 mg-S L⁻¹, which corresponded to an equilibrium concentration of gaseous H₂S at 400–1000 ppm (pH 2-10) (Jensen et al. 2011). Liquid samples
were taken at 15 minute intervals during the first hour and then every 1-hour over 4 hours for the analysis of inorganic sulfur compounds using ion chromatography (Dionex ICS-2000)(Keller-Lehmann et al. 2006).

3. Results and discussion

3.1. Corrosion of concrete coupons exposed in the gravity sewer

3.1.1 Visual inspection, surface pH and corrosion rate

During the exposure period, the gaseous H₂S concentration inside the pipe was at 1100±100 ppm, the temperature was 21.5± 2.4 ºC, and the relative humidity was 95.7 ± 3.0%. This level of H₂S inside the pipe represented high level hot spots that occur in sewers. The high level also facilitated the observation of measurable corrosion within a reasonable timeframe (i.e. exposure time of several weeks).

From visual inspection, before exposure, the grayish surface of all four coupons was smooth and firm (Figure 2). After 20 days, the color of entire surface became darker and obvious corrosion products were observed at the edge of coupons (Figure 2). The corrosion products were a light yellow color, expansive and loose. This is similar to typical corrosion products formed due to microbial induced corrosion (Cayford 2012). The middle part of each coupon was still sound with some dark spots observed from visual inspection. Likely the darks spots were attributed to the leaching of ferruginous components of aggregates (Jana and Lewis 2005).
Figure 2. The surface conditions of the four concrete coupons before exposure (the first row), and after 20-days exposure (the second row).

Regional differences regarding pH was also observed on these coupons. The surface pH of coupons reduced from 10.5±0.3 to 3.1±0.5 at the edge and to 7.7±0.1 in the middle parts after 20 days of exposure in the pipe. Surface pH is usually regarded as a good indicator of corrosion development and mass loss of concrete, as the alkalinity of the exposed concrete surface is consumed by direct or indirect reaction with H₂S in the sewer atmosphere. In a real sewer with 423 ppm of H₂S, the surface pH dropped from c.a. 10 to c.a. 7 in 6 months then further reduced to c.a. 4 in 20 months (Wells and Melchers 2015). Another lab study found that the surface pH was reduced from c.a. 10 to c.a. 7 and c.a. 4 in 6 months and 24 months exposure to 50 ppm of H₂S, respectively (Jiang et al. 2015b). In comparison, the reduction of surface pH on both the middle and edge parts of the concrete coupons were much faster in this study. The pH reduction of concrete would eventually lead to the loss of concrete (Islander et al. 1991).

The average corrosion rate was determined from the four coupons as 3.5± 0.3 mm year⁻¹ during the 20 day exposure. Consistent with the pH and visual inspection, the corrosion rate is not uniform on the surface of each coupon. The corrosion on about 40-60% area of each coupon was observed to be insignificant (Figure 3). Whereas, several peaks of higher corrosion rates
on less than 10% area of each coupon, were observed at around 9 mm year\(^{-1}\), 2-5 mm year\(^{-1}\), around 7 mm year\(^{-1}\) and around 5 mm year\(^{-1}\) for coupon I, II, III and IV, respectively (Figure 3). These higher corrosion rates were observed on areas along the edges of the coupons. As a combination of cement, water, aggregates and other admixtures, concrete is not a homogenous material. The structure of concrete around the edge is likely to be less sound due to the density gradient of cement and aggregates, in comparison to the middle parts of the coupons. Additionally, areas along the coupon edges on the surface were likely subjected to corrosion attack from both the exposure surface and from the sides of exposure surfaces.

![Relative frequency distribution of corrosion rates on the exposed surface of the four coupons (I, II, III and IV)](image)

**Figure 3.** Relative frequency distribution of corrosion rates on the exposed surface of the four coupons (I, II, III and IV)

The average corrosion rate observed was similar to the rates detected on pipes subjected to corrosion in the USA, and higher than the rate of a sewer pipe with 12 years exposure, that is reportedly due to microbial induced corrosion (Zhang et al. 2008, Mori et al. 1991). The coupons used in this study were produced from fly ash blended concrete. Fly ash blended concretes are reported to be resistant to sulfide-oxidizing bacteria and have lower corrosion rates (1.0–1.3 mm year\(^{-1}\)) . The corrosion rate detected in this study, especially on the coupon edge areas, was higher than that previously reported for fly ash blended concrete and for most
sewer corrosion studies (Zhang et al. 2008, Mori et al. 1991). Furthermore, in studies of microbial induced concrete corrosion, the corrosion rates are usually reported after an initiation period. The initiation of corrosion on new concrete was conventionally considered as a slow process that takes several years or decades (Joseph et al. 2012). For example, corrosion loss was only observed after 12-months exposure in a real sewer with H$_2$S concentrations as high as 423 ppm and after 34-months exposure in a laboratory corrosion chamber with 50 ppm H$_2$S (Jiang et al. 2015b, Wells and Melchers 2015). The fast corrosion that developed within 20 days in this study was different from all the previous reports.

The visual inspections, pH reduction and the determined corrosion rates confirmed the rapid development of corrosion on the coupon surface. This differs to what is previously reported and this rapid corrosion was very likely due to the extremely high concentration of H$_2$S, which facilitated the chemical oxidation of sulfide.

3.1.2 Corrosion product characteristics

The microstructure analysis using SEM revealed considerable mineralogical changes on the coupon surface. Angular crystal formations were observed to be sulfur-containing corrosion products (Figure 4A, Figure S2) (Cayford 2012). These corrosion products were either loosely scattered on fly ash (region 1, Figure 4A) (Kutchko and Kim 2006), or piled up on a cement matrix (region 2 and 3, Figure 4A). Hexagonal formations (region 3, Figure 4A) and a collection of amorphous particles (region 2, Figure 4A) were observed, and these were typical of hydration products of cement, cement-calcium hydroxide, and calcium silicate hydrate (Franus et al. 2015). Lesser amounts of those hydration products were observed in comparison to corrosion products, which suggests that alkalinity loss occurred due to the corrosion process. Similar microstructure was observed for all these four coupons (i.e. coupon I, II, III and IV) (Figure S2). In microbially induced concrete corrosion, microbial cells are detected by SEM
as small elongated shapes in the corrosion layer (Cayford et al. 2017). In this study, no evidence of microbes was found in the corrosion layer (Figure 4A, Figure S2).

![Image of corrosion products](image)

**Figure 4.** A SEM image of corrosion products on the surface of coupon I after the 20-day exposure in the pilot gravity sewer pipe (A), sulfur species in the corrosion products (B), BSE image indicating the regions on the coupon I surface selected for EDS analysis, shown as SPEC 1, 2 and 3 (C), and the percentage of elements by weight, except the coating material, of SPEC 1, 2 and 3 (D).

Based on the different regional brightness in BSE images (Figure 4C, Figure S2), the major elements, minus the coating material, were detected at the typical spots for each coupon (i.e. SPEC1, 2, 3) by EDS analysis (Figure 4C, D). The corrosion products, formed in the angular shapes (SPEC 1, Figure 4C), mainly consisted O, Ca and S with the atomic ratio of 6.3: 0.9: 1.0 (O: Ca: S). This suggests that the angular crystal corrosion products is mainly gypsum.
(CaSO$_4$·2H$_2$O), a typical corrosion product in microbial induced concrete corrosion (Grengg et al. 2015, Gutierrez-Padilla and Dolores 2007). Similar to SEM images, the corrosion products were piled up on calcium hydroxide (hexagonal formations) in SPEC 2 and calcium silicate hydrate (a collection of amorphous particles) in SPEC 3 (Figure 4 C), where the calculated atomic ratios were 7.1: 0.8: 1.0 (O: Ca: S) and 10.1: 0.7: 1.0: 0.5 (O: Ca: S: Si), respectively. Although the atomic ratio varied depending on the associated hydration products, the O/S ratio, and the soluble sulfur species analysis of the corrosion products collected from each coupon surface, further confirmed that sulfate was the dominant product of the H$_2$S oxidation with some elemental sulfur present in the corrosion product (Figure 4B).

Previously, elemental sulfur was the main product in the initiation stage in laboratory chamber experiments, where it was reported that the abiotic process of concrete corrosion mainly occurred (Jiang et al. 2015b, Joseph et al. 2012). Sulfate was only detected in corrosion products after twelve-month exposure in a laboratory chamber with 50 ppm of gaseous H$_2$S (Jiang et al. 2015b, Joseph et al. 2012). During the initiation stage, the maximum amount of sulfate was reposted as 2.2 g m$^{-2}$ after twelve months exposure, while the levels of elemental sulfur were more than an order of magnitude higher (Joseph et al. 2012). In contrast, the sulfate content of corrosion products on the whole coupon surface in this study were 2-3 times higher than elemental sulfur and were two times higher than the maximum concentration reported in the laboratory chamber study (Joseph et al. 2012) (Figure 4B).

The observed rapid corrosion and the formation of sulfate as the main corrosion products cannot be explained by either the three-stage corrosion development model (Islander et al. 1991) or the previous theory describing the initiation of corrosion (Jiang et al. 2015b, Joseph et al. 2012). The short exposure time suggests that there was likely no development of any sulfide oxidizing microorganisms. Instead, fast chemical oxidation of H$_2$S to sulfuric acid might be the main cause of the observed fast corrosion and sulfate dominated corrosion products.
3.2. Microbial community in the corrosion layer

To delineate the role of microbes in the observed rapid corrosion, the microbial communities were determined for the combined corrosion layer collected from the four coupons (CA, CB) and from wastewater samples (WA, WB) (Figure 5). In the corrosion layer, *Bacteroides*, *Prevotella*, *Barnesiella*, *Faecalibacterium*, *Streptococcus*, *Christensenellaceae R-7 group*, and *Caulobacter* were detected as the top 8 abundant microbes. Most of these bacteria detected are anaerobes and none of them are known to be capable of oxidizing sulfur. *Bacteroides*, *Prevotella*, *Barnesiella* and *Faecalibacterium* are obligate anaerobic bacteria, and are found prominently in human guts (Bernhard and Field 2000, Ramirez-Farias et al. 2008, Wu et al. 2015). Most *Streptococcus* are facultative anaerobes and are mostly related to infection of human and animals (Cleary et al. 1992). *Firmicutes* are anaerobic microbes and found in various environments including human guts and fuel cell experiments (Ismail et al. 2011, Wrighton et al. 2008). *Christensenellaceae R-7 group* are anaerobic bacteria that can be found in the ruminal mucosa of goats and food waste digester (Jiao et al. 2018, Lee et al. 2017). *Caulobacter* are generally aerobic microbes detected in a dilute aquatic environments with limiting nutrients (Ely 1991). Based on the probable capabilities of these bacteria detected in the oxidative corrosion layers, there is little to suggest they were active components. It is likely we are detecting the remnants of bacteria that have come from the wastewater.
Figure 5. Heatmap summarizing the percent relative abundances of bacteria (each row representing an OTU) in the corrosion layer samples combined from the four coupons (CA and CB). Two wastewater samples from the same sewer pipe was included as WA and WB. Reads that could not be classified are collectively referred to as ‘unclassified’.

In microbial induced concrete corrosion, once the pH is reduced to lower than 4, due to the sulfide oxidation and acid production, acidophilic microbes usually become the dominant species (>50%). The most typical genus of acidophilic microorganisms associated with biogenic acid production is *Acidithiobacillus* including *A. ferrooxidans*, *A. thiooxidans*, and *A. caldus* (Davis et al. 1998, Harrison Jr 1984, Islander et al. 1991, Jiang et al. 2016b, Parker 1945b). In addition to *Acidithiobacillus spp.*, *Acidiphilium spp.*, *Mycobacterium spp.*, *Xanthomonadales spp*, are often detected as abundant in acidophilic communities of sewer corrosion layers (Cayford et al. 2017, Jiang et al. 2016b, Li et al. 2017, Okabe et al. 2007, Pagaling et al. 2014). None of these typical acidophilic sulfur-oxidizing microorganisms was detected in the corrosion products collected from the concrete samples in this study. Therefore, it is highly likely that biological sulfide oxidation was not playing a major role in the rapid corrosion observed in the presence of high H₂S levels.
3.3. Sulfide oxidation rates of the concrete coupons after exposure

The SOR of the coupons prior to and after sterilization were quite similar for H$_2$S concentrations up to 200 ppm (Figure 6). It shows clearly that sterilization of the concrete did not have any impact on the SOR and it confirms that the microbes on the concrete had negligible role in H$_2$S oxidation. Together with the absence of sulfide oxidizing microbes in the corrosion layer (Section 3.2), it clearly suggests that biological sulfide oxidation is not the cause of the concrete corrosion and thus the SOR observed were mainly due to chemical oxidation of sulfide.

![Figure 6](image_url)

**Figure 6.** Sulfide oxidation rates of concrete coupons before and after sterilization under 10-200 ppm H$_2$S (A), and the sulfide oxidation rates of concrete coupons under 500-1500 ppm H$_2$S (B).

The SOR of both coupons were below 25 mg-S m$^{-2}$ h$^{-1}$ under 10-200 ppm H$_2$S and increased to around 200 mg-S m$^{-2}$ h$^{-1}$ at approximately 1500 ppm H$_2$S. The SOR observed for the chemical oxidation process is comparable to the sulfide uptake rate (SUR). SUR is usually used as a good indicator for the development and activity of sulfide oxidizing bacteria in microbial induced concrete corrosion. The SUR of 250 ± 5 mg-S m$^{-2}$ h$^{-1}$ was reported for microbial induced corrosion after 33 months exposure to H$_2$S at 50 ppm (Sun et al. 2014) and around 100 mg-S m$^{-2}$ h$^{-1}$ for coupons after 17 months exposure under 25 ppm H$_2$S (Jiang et al. 2016b). At the exposure of 1000 ppm of H$_2$S, a rapid consumption of H$_2$S, 3600 mg-S m$^{-2}$ h$^{-1}$ was
observed in a pipe section after several months (Vollertsen et al. 2008). Under the same H\textsubscript{2}S concentration, the SOR measured in this study was relatively lower compared with previous studies reported for microbially induced corrosion. However, the SOR at above 1000 ppm H\textsubscript{2}S of this study were comparable to the uptake rate of microbes under 50 ppm (Sun et al. 2014), which could lead to similar magnitudes of corrosion.

Under the high levels of H\textsubscript{2}S (500ppm-1500ppm), the SOR increased significantly along with the increase of H\textsubscript{2}S concentration (Figure 6B). Kinetic models (i.e. exponential, power), have been previously used to describe the oxidation rate of sulfide in microbially induced concrete corrosion (Æsøy et al. 2002, Sun et al. 2014). Fitting SOR results into exponential kinetics, the exponent showed a positive value (0.0021) (Figure 6B), which is contrary to the negative value previous reported for microbial corrosion (-0.0135) (Sun et al. 2014). In power kinetic models, the reaction order for sulfide oxidation in this study was estimated to be 2.4, which is higher than the reaction order (1.5) previously reported for chemical dominated sulfide oxidation on concrete surfaces and also higher than that reported for microbial induced sulfide oxidation on corroding concrete surfaces (0.45-0.7) (Satoh et al. 2009, Vollertsen et al. 2008). With the highest $R^2$ (0.995) and lowest sum of residual squares (323.2), exponential kinetics best described the chemical sulfide oxidation on the concrete surface in this study (Table S2). The kinetic analysis suggested that chemical sulfide oxidation is different to the biological sulfide oxidation and that the SOR increases exponentially with H\textsubscript{2}S concentration, implicating that chemically induced corrosion will be more severe in sewers with higher H\textsubscript{2}S concentrations.

3.4. Chemical oxidation of sulfide in the presence of concrete or corrosion products

In the batch tests with aerated water containing fresh concrete powder, more than 70% of the sulfide was oxidized within 4 hours (Figure 7A) and the total amount of inorganic sulfur species remained constant (Figure S4). The main oxidation products were found to be sulfate and
thiosulfate, accounting for 52.6±0.8 % and 42.0±1.3 % of the total oxidized sulfide, respectively. The molar consumption ratio of sulfide to oxygen was 0.8±0.1, which was consistent with the theoretical oxygen demand ratio for the production of sulfate and thiosulfate. During the 4 hour batch tests, the production of elemental sulfur was not observed. The average sulfide oxidation rate was 1.12 ± 0.01 mg-S L⁻¹ h⁻¹ and the pH was stable at 11.3±0.1 during the whole process. This relatively stable pH is consistent with the strong acid neutralization capacity of concrete powder within the range of pH 13-10 (Figure S3).

Figure 7. Chemical oxidation of sulfide in aerated water containing fresh concrete powder (A) and autoclaved corrosion layer scrapings (B).

For the batch tests containing autoclaved corrosion layer scrapings, 26% of the sulfide dosed was oxidized during the tests (Figure 7B). Along with the sulfate production, the elemental sulfur from the corrosion product was reduced by 35%±5%. The molar consumption ratio of sulfide/oxygen was 1.7±0.1 and the total amount of inorganic sulfur species remained constant. Considering elemental sulfur oxidation and potential formation of polysulfide between elemental sulfur and sulfide, it was unclear whether sulfate production is due to the oxidation of elemental sulfur or sulfide. However, the average sulfide oxidation rate, 0.22±0.02 mg-S L⁻¹ h⁻¹, was 5 times lower than the batch tests with fresh concrete powder. Production of sulfite and thiosulfate was not observed over 4 hours and the pH was 2.58±0.09 during the whole
In previous batch tests, the chemical sulfide oxidation rate in acidic solutions (pH<2) of suspended corrosion products was reported as 0.01-0.1 mg-S L⁻¹ h⁻¹ and elemental sulfur was assumed to be the main product as deduced from the oxygen and hydrogen sulfide uptake ratio (Jensen et al. 2011). The chemical sulfide oxidation in solutions of crushed new concrete with high alkalinity has not been reported. For the chemical oxidation of sulfide tests in water, thiosulfate is found as the principal product at pH>8.5, regardless of the sulfide/oxygen ratio, and the oxidation products were not reported at pH<6, since the oxidation rate was very slow (Chen and Morris 1972). In this current study, the production of sulfate by chemical oxidation of sulfide in solutions containing either fresh concrete powder or corrosion product was observed and confirmed by direct measurement for the first time. Possibly the reactions observed here are due to metals such as Fe²⁺, Fe³⁺ and Cu²⁺, existing in the concrete and corrosion product and catalyzing the chemical oxidation of sulfide. The higher oxidation in fresh concrete solutions suggested more significant impact due to chemical oxidation of sulfide on the concrete corrosion process. Therefore, with sulfuric acid as the main product, chemically induced corrosion of concrete under high H₂S concentration in sewers plays a critical role, especially for newly manufactured concrete sewers.

4. Conclusions

The rapid corrosion of fresh concrete within 20 days at high hydrogen sulfide concentration in sewers was investigated. Different from previous studies, which mainly focus on microbially induced corrosion of concrete sewers, this was the first-ever report of chemically induced corrosion. This has resulted in the following key findings:

- Hydrogen sulfide of around 1000 ppm led to fast concrete corrosion within one month, this was characterized by a surface pH around 3 and a corrosion rate around 3 mm year⁻¹.
The fast corrosion of concrete with high levels of H$_2$S in the sewer was mainly due to the chemical oxidation of hydrogen sulfide to sulfuric acid. No sulfide oxidizing microorganisms were found to participate in the corrosion.

The rate of chemical sulfide oxidation increased exponentially with hydrogen sulfide concentrations and this could induce potentially high corrosion rates.

These novel findings of in-sewer corrosion processes hold profound implications for sewer operation and corrosion management. The chemically induced corrosion of newly manufactured concrete sewers would be critical when high H$_2$S concentrations occur in the sewer atmosphere, especially at certain corrosion hot spots.

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Reference:


