Mechanisms and Processes of Concrete Corrosion in Sewers

Xuan Li, Guangming Jiang, Cyrill Grengg, and Florian Mittermayr

Abstract Concrete corrosion in sewers is caused by the combination of chemical and biological processes including sulfide and carbon dioxide generation and partition in wastewater, sulfide oxidation, neutralizing reactions of carbon dioxide, hydrogen sulfide, and its oxidation products (mainly sulfuric acid) with concrete. Wastewater is a sulfate-rich environment with sufficient carbon sources. The metabolism of sulfate-reducing bacteria leads to the formation of hydrogen sulfide in wastewater under anaerobic conditions. During wastewater transport through the sewers, depending on the dissolved oxygen concentrations and pH in wastewater, hydrogen sulfide can be chemically or biologically oxidized in wastewater, or partition into sewer gas in gravity sewers. Due to the alkaline and porous nature of concrete sewer pipes, the hydrogen sulfide reacts with intact concrete and reduces the concrete pH, lowering the concrete surface pH through chemically induced corrosion. The additional outgassing of CO_2 from the wastewater further accelerates these processes. The reduction of surface pH facilitates the colonization of sulfide-oxidizing microorganisms on concrete surfaces. Sulfide-oxidizing microorganisms can further biologically

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X. Li · G. Jiang (✉)
School of Civil, Mining, Environmental and Architectural Engineering, University of Wollongong, Wollongong, NSW 2522, Australia
e-mail: gjiang@uow.edu.au

X. Li
e-mail: xuan.li@uts.edu.au

X. Li
School of Civil and Environmental Engineering, Centre for Technology in Water and Wastewater, University of Technology Sydney, Ultimo, NSW 2007, Australia

C. Grengg
Institute of Applied Geosciences, Graz University of Technology, Rechbauerstraße 12, 8010 Graz, Austria
e-mail: cyrill.grengg@tugraz.at

F. Mittermayr
Institute of Technology and Testing of Building Materials, Graz University of Technology, Inffeldgasse 24, 8010 Graz, Austria
e-mail: f.mittermayr@tugraz.at

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oxidize hydrogen sulfide into sulfuric acid, leading to microbiologically influenced concrete corrosion. This chapter describes and discusses the mechanisms of these processes in sewers.

1 The Sulfur Cycle in Sewers

As described in Chapter "Concrete Sewer Systems and Wastewater Processes Related to Concrete Corrosion", modern sewers majorly consist of two types of sewers: rising main and gravity sewers. In rising main sewers, pipes are fully filled with wastewater and operated with no gas phase under anaerobic conditions. In some cases, at the entry of the rising main sewers, there will be an aerobic phase but along the distance in the pipe, the wastewater becomes anoxic [14], and anaerobic due to the consumption of oxygen as the electron acceptor for microbial processes [21]. Gravity regions are usually partially filled, where wastewater flows downstream due to gravity. In gravity sewers, both aerobic and anaerobic conditions can occur below the water surface depending on the wastewater temperature, turbulence and flow rates of the wastewater (i.e. determined by the slope, size of the pipe, and hydraulic load), ventilation (i.e. either natural or forced) and the water depth-to-diameter ratio of gravity sewers [1, 20]. The rising main sewer contains four main components: (1) wastewater; (2) biofilms; (3) sewer sediments; (4) sewer walls. While gravity sewers contain all these four components with one additional important component: the sewer gas.

Within the sewer system, the sulfur cycle is one of the most complex nutrient cycles. Wastewater is inherently a sulfate-rich environment, where the concentration of dissolved sulfate is typically 20–200 mg-S/L in wastewater [47]. The major source for this high sulfate concentration was identified as the coagulant used for the production of drinking water (52%), source water (38%), and other human wastes [37]. The change of sewer conditions alters the electron acceptors for chemical and biological reactions and products. Due to the dissolution and oxidation of sulfide, various sulfur compounds exist in sewers (Table 1).

Table 1 Inorganic sulfur species and the sulfur oxidation states adapted from Suzuki [42]

Oxidation state				
− 2	0	+ 2	+ 4	+ 6
H_2S hydrogen sulfide	S^0 elemental sulfur	(SO) sulfur monoxide	SO_2 sulfur dioxide	SO_3 sulfur trioxide
HS^- bisulfide		H_2SO_2 sulfoxylic acid	H_2SO_3 sulfurous acid	H_2SO_4 sulfuric acid
		$S_2O_3{}^{2-}$ thiosulfate	$SO_3{}^{2-}$ sulfite	$SO_4{}^{2-}$ sulfate
		$S_4O_6{}^{2-}$ tetrathionate		

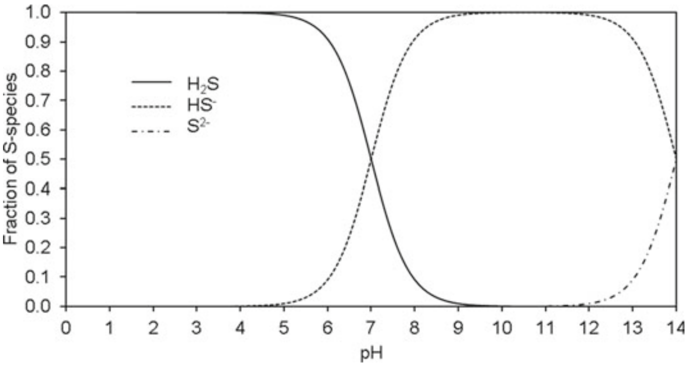

Fig. 1 The impact of the wastewater pH on the dissolved sulfide speciation (pKa_1 of 7 and pKa_2 of 14)

For both abiotic and biotic reactions, water is the major medium that allows the reaction to happen. In anaerobic parts of sewers (i.e. rising main sewer and anaerobic part of gravity sewer), sulfate becomes the main electron acceptor, where hydrogen sulfide is biologically produced by sulfate-reducing bacteria (SRB) [10]. In rising main sewers, the oxidation of sulfur happens in the wastewater phase; while in gravity sewers, it can occur in both the wastewater phase and moist sewer pipe surfaces in contact with oxygen [22]. Under both conditions, the dissociation of hydrogen sulfide is crucial for the distribution and oxidation of sulfide species, primarily controlled by the pH of the system. As described in Chapter "Concrete Sewer Systems and Wastewater Processes Related to Concrete Corrosion", sulfide is a weak acid with pKa_1 value of 7 and pKa_2 value ranging from 11.96 to 17.00 [10, 36]. The pH dependent dissociation of hydrogen sulfide is shown in Fig. 1.

In normal wastewater conditions (7.5–8.5), bisulfide is the dominant sulfide species (Fig. 1). The main products of chemical sulfide oxidation with oxygen are thiosulfate ($S_2O_3{}^{2-}$) and sulfate ($SO_4{}^{2-}$), depending on the availability of oxygen in wastewater [32]. When oxygen is limiting, thiosulfate is the main product. The further oxidation of thiosulfate to sulfate mainly takes place in sewer pipes with long hydraulic retention times (HRT) [31]. Chemical oxidation of sulfide with oxygen also produces common intermediates such as elemental sulfur (S^0) and sulfite ($SO_3{}^{2-}$) [18]. The latter is rapidly oxidized by oxygen to sulfate and is often negligible in wastewater. Elemental sulfur, thiosulfate, sulfite, and sulfate are formed according to Eqs. (1)–(4) [31]:

$$2HS^- + O_2 \rightarrow 2S^0 + 2OH^- \quad (1)$$

$$2HS^- + 2O_2 \rightarrow S_2O_3^{2-} + H_2O \quad (2)$$

$$2HS^- + 3O_2 \rightarrow 2SO_3^{2-} + 2H^+ \quad (3)$$

$$2HS^- + 4O_2 \rightarrow 2SO_4^{2-} + 2H^+ \qquad (4)$$

Temperature and pH are important parameters affecting the abiotic oxidation of sulfide in aqueous environments. Studies performed on inactivated wastewater showed that chemical sulfide oxidation rates increase with increasing temperature [5, 32]. The pH of the solution also showed a significant impact on the abiotic oxidation process [5]. In acidic solutions with $pH < 6$, where H_2S is the predominating sulfide species (Fig. 1), the chemical oxidation rate of sulfide is very slow. The specific rate increases greatly as pH increases through 7 to a maximum of pH 8.0, then decreases to a minimum near pH 9, increases again to a second maximum about equal to first near pH 11, and finally decreases again in more alkaline solutions [5]. Similarly, a reaction pattern is also observed in [27], where the half-time ($t_{1/2}$) for the oxidation of H_2S by O_2 is estimated as 50 ± 16 h at 26 ± 9 °C in water with a pH of 8. Thus, the chemical oxidation of sulfide is generally considered a slow process.

In aqueous environments, biological sulfide oxidation can occur by sulfur-oxidizing microorganisms (SOM) at a faster rate than chemical oxidation [10]. Biological sulfide oxidation in the solution mainly occurs when sulfide generated in the upstream sections (i.e. rising mains) is transferred to the aerobic sections (i.e. gravity sewers) or when sulfide generated in the anaerobic part of biofilms diffuses to the aerobic part of biofilms [10]. The oxidation products are impacted by the sulfide and dissolved oxygen (DO) concentration. Under limited DO conditions, sulfide in water is oxidized by SOMs to elemental sulfur [30]. When DO concentration is sufficient, besides elemental sulfur, sulfate can be produced by SOM with thiosulfate, thrithionate, and tetrathionate as intermediates [35]. High concentrations of sulfide are toxic to some SOM [3]. Although elemental sulfur can be produced in both chemical and biological reactions, it is worthy to note that the elemental sulfur produced from chemical oxidations of sulfide is hardly used by SOMs [11]. This might be related to the particle size and surface properties of the elemental sulfur produced. In particular, the elemental sulfur produced by abiotic oxidation of sulfide is found quite hydrophobic but biologically produced elemental is hydrophilic, which is easier for the colonization and development of SOMs [19].

When the DO concentration is insufficient (normally < 0.5 mg/L) for either abiotic or biotic oxidation of sulfide, sulfide start to accumulate in the wastewater, which eventually leads to the partition of hydrogen sulfide to sewer gas in gravity sewers [10]. Among the sulfide species (Table 1), hydrogen sulfide is the only specie that can partition into the sewer gas phase. Hydrogen sulfide is moderately soluble in water ranging from 4 g/L at 20 °C to 6.3 g/L at 4 °C [2]. The partition process of H_2S is highly pH dependent. As shown in Fig. 1, at pH values below 8, hydrogen sulfide will present and can partition into the headspace [33]. Lower wastewater pH leads to a higher hydrogen sulfide release into the sewer atmosphere. Generally, Henry's law describes the partition of gases across the air–water interface. However, this steady state relationship does not apply to the dynamic partition of sulfide into the sewer atmosphere due to ever-changing conditions such as the occurrence of ventilation (either natural or forced), intermittent wastewater flow, and turbulence in sewer systems. Furthermore, the overall mass transfer increases with higher temperature, thereby resulting in an increase in the ratio between hydrogen sulfide concentrations in the gas phase and in the liquid phase [4]. More importantly, the emission and subsequent oxidation of H_2S also leads to the chemically and microbiologically influenced corrosion in gravity sewers, which significantly shortens the service life of sewer pipes [13]. The details of chemically and microbially influenced corrosion are discussed in the following sections.

2 Chemically Induced Concrete Corrosion

2.1 The Impact of Corrosive Environment in Sewers

The corrosion of concrete in the sewer environment is attributed to two parts: the corrosive environment in sewers (i.e., H_2S, CO_2, relative humidity, wastewater etc.) and the physical and chemical properties of concrete. As mentioned in Chapter "Concrete Sewer Systems and Wastewater Processes Related to Concrete Corrosion", concrete is a multicomponent, inorganic, porous material which for the most parts consist of the hardened cement paste and aggregates. The hydrated cement paste forms a network of hydration products consisting of calcium silicate hydrates (C–S–H), calcium hydroxide (CH) and minor quantities calcium aluminates (AFm) and ettringite (Aft) [7, 43].

The pH of the pore solution of hardened concrete made from OPC is usually > 13 [16, 43, 44]. Little microbial activity occurs at this stage due to the prevailing high alkalinity. According to the three-stage theory [11], this phase is named the initial acidification stage, where the pH is abiotically reduced from ~ 13 to ~ 9 through carbonation and hydrogen sulfide dissolution, within the condensate of the surface near pore structure.

The carbonation of the concrete surface starts from the manufacturing time of concrete sewer pipes. Directly contacted with the surface of concrete pipes or absorbed in pores, CO_2 reacts with calcium hydroxide and hydrated calcium silicate (C–S–H) in concrete and produces calcium carbonate (Eqs. 5 and 6) [9].

$$\mathrm{Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O} \tag{5}$$

$$\mathrm{C{-}S{-}H + CO_2 \rightarrow CaCO_3 + SiO_2 + H_2O} \tag{6}$$

In a laboratory test setup with 5–50 ppm H_2S, 18–30 ºC, and 85–100% relative humidity, it was shown that carbonation decreases the surface pH from 13 to about 10 [17]. Then, H_2S had a significant role in the initial abiotic pH reduction, and directly reacts with $Ca(OH)_2$ in concrete (Eq. 7), which further reduces the pH of concrete to around 8.

$$Ca(OH)_2 + 2H_2S \rightarrow Ca(HS)_2 + 2H_2O \quad (7)$$

In contrast, on-site measurements within several corroded sewer basins in Austria reported high CO_2 concentrations of up to 6500 ppm, implying a central role of CO_2 within the initial abiotic pH reduction of concrete due to ongoing carbonation of the cementitious matrix [8]. The diffusion of CO_2 into the pore solution triggers a dissolution of $Ca(OH)_2$, Ca depletion of the C–S–H phases and concurrent formation of calcium carbonates. Described chemical reaction are accompanied with a pH reduction to as low as 8.0. In this context the overall impact of CO_2 on the corrosion process is strongly associated with the overall relative humidity and corresponding water saturation of the pores since strongly controlling the diffusion kinetic of CO_2. Accordingly, carbonation induced pH reduction may dominate in systems exhibiting lower relative humidity levels and/or high daily and/or seasonal changes in relative humidity (e.g. sewer manholes vs. sewer pipes).

Apart from direct reactions between corrosive sewer gases (i.e. CO_2 and H_2S) with concrete, due to the presence of oxygen, H_2S can be chemically oxidized on concrete surfaces. To date, the understanding of abiotic/chemical sulfide oxidation on concrete surfaces is limited. Few studies have investigated the chemical oxidation of H_2S on concrete surfaces. In laboratory-controlled corrosion chambers with H_2S below 50 ppm, elemental sulfur was found as the major oxidation product, with the presence of sulfate (< 10%) [17]. The oxidation of H_2S may thus occur according to Eq. (8) or Eq. (9).

$$Ca(HS)_2 + O_2 \rightarrow 2S + Ca(OH)_2 \quad (8)$$

$$2H_2S + O_2 \rightarrow 2S + 2H_2O \quad (9)$$

In sewer systems affected by MICC, the reduction of pH during the initiation stage is usually followed by the development of biofilms on the concrete surfaces and corresponding biologically controlled sulfur oxidation reactions [11]. However, in systems exhibiting very high H_2S concentrations chemical oxidation of H_2S may remain the dominant process of concrete deterioration. Within a pilot-scale study with gaseous H_2S concentrations of 1100 ± 100 ppm, concrete samples were rapidly corroded in 20 days. The initial surface pH > 10 was rapidly reduced to around pH 3. Newly formed Ca-sulfate precipitates were identified as the main corrosion products [24]. This rapid corrosion was found to be caused by the chemical oxidation of H_2S to sulfuric acid. The fast and direct formation of sulfate through abiotic sulfide oxidation under alkaline conditions was further confirmed by aerated water containing fresh concrete powder, where more than 70% of the sulfide was oxidized within 4 h in this study. The sulfide uptake test of the concrete coupon further revealed that the chemical sulfide oxidation on the concrete surface followed exponential kinetics at H_2S concentration between 500–1500 ppm [24]. However, with ongoing pH reduction towards acidic conditions, the chemical oxidation rate of sulfide was found to slow down due to the formation of corrosion layer [24]. Thus, this rapid chemically induced corrosion is likely still serving as a precedent stage for the development of advanced microbial corrosion, which requires future investigations. In real sewers, the H_2S concentration varies from several ppm to hundreds of ppm [22]. Such high concentrations H_2S (i.e. 500–1000 ppm) has been frequently detected in many sewers, which potentially accounts for higher corrosion rates than previously assumed [46]. Therefore, chemical concrete corrosion due to the interaction with H_2S and CO_2 can be an important deterioration process in sewers.

In regard to the factors affecting the chemically induced corrosion, H_2S concentration played an important role in both studies as mentioned above, where a quicker pH reduction and higher amount of corrosion products (sulfide oxidation products) were observed under higher H_2S concentrations [17, 24]. In the laboratory study, higher temperature, and relative humidity also facilitate the corrosion process [12, 15, 17]. As detailed in Sect. 1, the chemical oxidation of H_2S in water is enhanced under higher temperatures. Furthermore, a higher temperature in sewer gas is also associated with a higher water evaporation rate, which together with relative humidity impacts the moisture level and condensation water layer on concrete (Sect. 1).

2.2 The Impact of Concrete Properties

Concrete is a porous material (Fig. 2a). Accordingly, the pore structure and volume play an essential role in respect to the material response within diffusion-based deterioration processes [34, 39]. The formation of the pore structure in concrete is closely related to the hydration processes of concrete. The hydration process is triggered once the cement is in contact with water and further developed during the curing process when concrete is fully immersed in water or water-based solutions (i.e., lime water). During the hydration process, the hydration products bind the aggregates with the cement matrix and occupy the pore spaces (i.e., the air voids introduced due to the mixing) (Fig. 2b). After the curing process, the hydration process continues until the excess water in the pores evaporates and leaves the pores empty or unsaturated.

The overall amount and structure of pores is controlled by the water to binder ratio (w/b), the cement chemistry and the curing conditions applied. Pores in concrete can be isolated or interconnected from one another. The interconnected pores are capable of transporting aggressive species, such as moisture, carbon dioxide (CO_2), and hydrogen sulfide within the cement paste, which thereby influences the corrosion development on concrete [26]. Based on the pore size distribution and relevant assumptions, Wells and Melchers [46] built a model for the relationship between concrete moisture level and relative humidity. It shows that the higher the relative humidity, the greater the increase of concrete moisture level, especially for the relative humidity range from 95 to 100%. At higher humidity levels, moisture in sewer gas condenses initially within the smaller diameter pores and then progressively

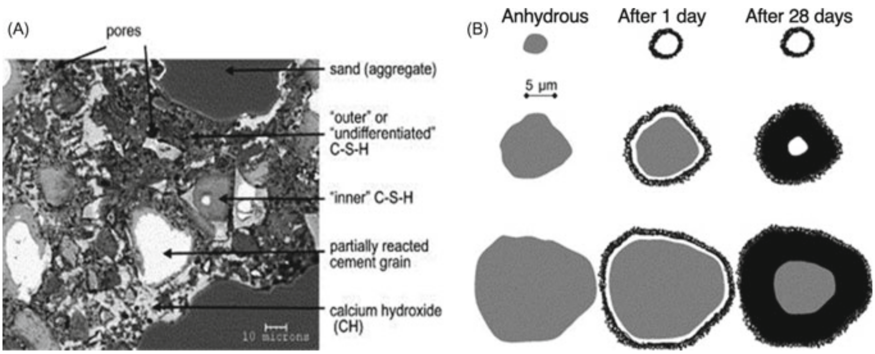

Fig. 2 **a** Backscattered (BSE) electron micrograph of an Ordinary Portland Cement mortar (200 days old, w/c = 0.4), with the microstructural constituents distinguished. **b** Schematic illustration of the formation of hydration shells according to grain size. Adapted from Scrivener [38] with permission from Elsevier

in larger diameter pores with further humidity increases until eventually, at 100% humidity, the pore space is fully filled. At this point, a condensate film forms on the concrete surface of the pipe [46]. Therefore, higher temperature and relative humidity in sewer gas allows an earlier and denser formation of condensation layer (as visually observed by Joseph et al. [17], which provides the suitable conditions for chemical oxidation of sulfide. In addition, the concrete chemical and physical properties are also dependent on the concrete materials and manufacture process, which subsequently affects the chemically induced corrosion [8, 25] (Fig. 3).

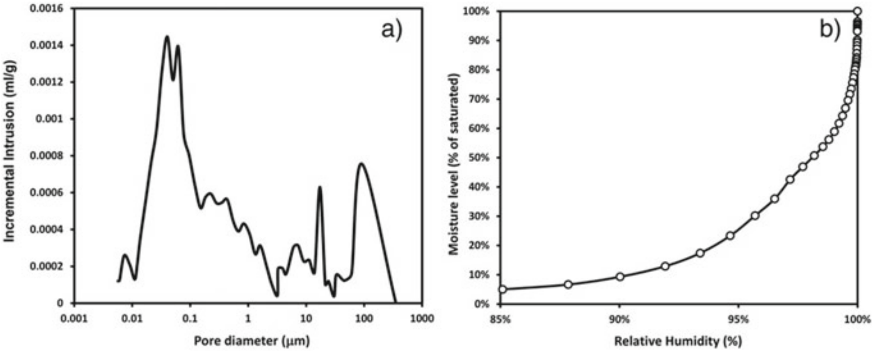

Fig. 3 **a** Pore size distribution of a concrete coupon and **b** the calculated response of concrete moisture level to changes in sewer gas relative humidity. Reproduced from Wells and Melchers [46] with permission from Elsevier

3 Microbiologically Influenced Concrete Corrosion (MICC)

Once the surface pH reaches about 9, neutrophilic sulfur-oxidizing microorganisms (NSOM) colonize the concrete surface [11]. NSOM are typical sulfur oxidizers that could biologically oxidize sulfur compounds to sulfuric acid. Sulfuric acid either produced by microorganisms or by chemical oxidization (discussed in Sect. 2) reacts with the cementitious phases and, if present carbonate aggregates, causing dissolution of the microstructure and the precipitation of expansive secondary minerals as Eqs. (10)–(13), where calcium sulfates (i.e., anhydrite, basanite and gypsum), ettringite and amorphous silica are found as the major corrosion products.

$$H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + H_2O \tag{10}$$

$$H_2SO_4 + C{-}S{-}H \rightarrow CaSO_4 + Si(OH)_4 + H_2O \tag{11}$$

$$H_2SO_4 + CaCO_3 \rightarrow CaSO_4 + H_2CO_3 \tag{12}$$

$$CaSO_4 + C_3A + H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \tag{13}$$

Continuous biotic acid production by NSOM lead to a further pH reduction within the corrosion horizons of the concrete to below 4. With the decrease of pH, the microbial community on the concrete surface gradually changes, which leads to the start of stage 3 of the corrosion. In stage 3, acidophilic sulfur-oxidizing microorganisms (ASOM) colonize and become the dominant microbe on the concrete surface, where the biological formation of large amounts of sulfuric acid occurs.

In contrast to chemically induced corrosion, numerous studies have investigated the development of microbiologically influenced concrete corrosion, where location, H_2S concentrations, relative humidity, temperature are found as critical factors affecting corrosion development in sewers. Depending on the availability of sewer gases and wastewater, MICC commonly occurs at two hot spots, namely crown regions and tidal regions in the sewer pipes (Fig. 4). Crown regions are the celling of the sewer headspace, while tidal regions are just above the wastewater flow level [22]. In manholes, corrosion also occurs in the regions next or the wastewater line (similar to the tidal regions), and manhole walls (similar to the crown regions). The availability of sewer gas and contact with wastewater varies greatly in these two locations. In crown regions, concrete contacts with wastewater very occasionally (e.g., during flooding), the sewer gases thereby become the major source of ‘food’ for microorganism development. The diffusion of gases (i.e., CO_2, H_2S, O_2) provides volatile substrates and nutrients for the development of NSOM and ASOM [12]. Furthermore, water content, a critical compound for microbial activities, is also provided by the moisture from sewer gas for crown regions. The water content in crown regions is majorly provided by the condensation from sewer gas with high relative humidity

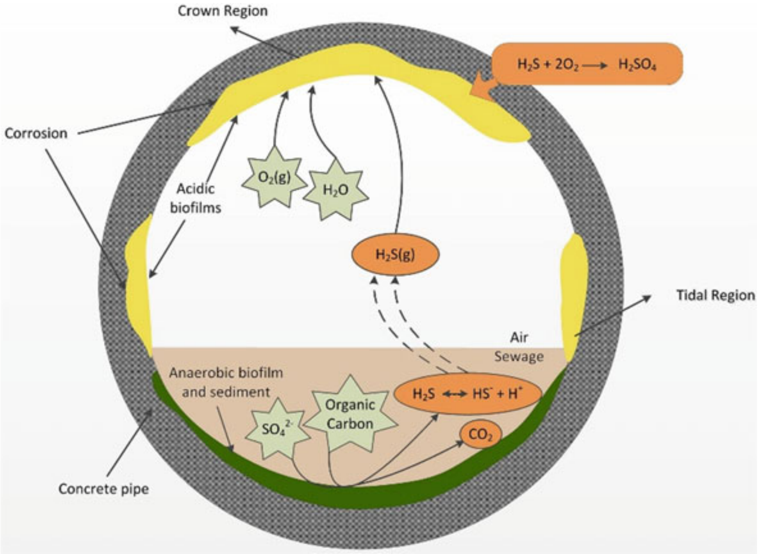

Fig. 4 A diagram of a cross-section of a sewer gravity concrete pipe summarizing the major processes that lead to the acid formation in the aerobic biofilms and the onset of sewer corrosion at two major hot spots, i.e., tidal and crown regions [22] (open access)

(as discussed in Sect. 2). In tidal regions, concrete walls receive frequent contact with wastewater, which provides the frequent replenishment of nutrients, microbial inoculum, and moisture. The abrasive effect of wastewater flow also removes the loss corroiosn layers [40]. This results in more severe corrosion in tidal regions than the crown regions [12, 29].

It has been observed for a long time that the microbiologically influenced corrosion was positively correlated with the H_2S levels in sewers globally. For instance, in the crown of a sewer in Japan with 5–400 ppm H_2S and 10–30 °C, the average corrosion rate was around 4.3–4.7 mm/year, but around 2 mm/year in another sewer with 10–50 ppm H_2S and 22 °C in Australia [28, 45]. However, these studies are commonly conducted in different sewers or laboratory setups, where other factors including the relative humidity, temperature, and the concrete type vary from study to study. This greatly hinders the understanding of the exact role of H_2S concentration in corrosion development. In the last decade, several well-controlled laboratory studies in conjunction with the field observations greatly improved the understanding of H_2S on corrosion development. In a laboratory study, the corrosion loss of concrete was found to follow the nth-order kinetics as Eq. (14).

$$C_r = k \times [\mathrm{H_2S}]^n \times f_{BET}(RH) + C_{ri} \tag{14}$$

where n is the model constant estimated from the experimental data; $f_{\mathrm{BET}}(\mathrm{RH})$ is a Brunauer–Emmett–Teller sorption isotherm of relative humidity and C_{ri} represents the corrosion caused due to historical exposure prior to the experiment. In this study, the *n* was estimated to around 0.5, suggesting a dominant role of H_2S concentration on the corrosion loss [12]. A similar observation was reported in a field study in Australia, where the corrosion rate followed *n*th order kinetics of H_2S concentration with an *n* value of 0.5–1.0 [45].

As discussed in Sect. 2, the increase of relative humidity and temperature facilitate the formation of a condensation layer on the concrete surface. Similar to the chemically induced corrosion, the increase of relative humidity enhanced the microbial development on concrete in crown regions [12]. While within tidal regions, where frequent wastewater contact is provided by the wastewater stream, the increase of relative humidity showed negligible impacts on the corrosion development [12]. Furthermore, as discussed in Sect. 2, the temperature increase also leads to faster biological oxidation of sulfide. Thus, the microbiologically influenced corrosion is found generally accelerated at higher temperatures. For instance, in sewer biofilms, the sulfide oxidation rates at 25 ºC were found to be about 15% higher than those at 20 ºC [41]. In laboratory-scale corrosion chambers with controlled conditions, the increase of temperature from 20 to 30 ºC also led to a faster acid generation and higher corrosion loss [12]. The details of SOM and their contributions to the microbiologically influenced corrosion will be further discussed in Chapter "Characterization of Corrosion Microbial Communities". In addition, the concrete chemical and physical properties also affects the MICC [6, 23].

4 Summary

This chapter discussed the mechanisms and processes involved in the corrosion of concrete sewers in the context of sulfur cycle and carbonation. The corrosion of concrete sewers is closely related to the corrosive environments in gravity sewers and the alkaline and porous nature of concrete. Wastewater is rich in sulfate and carbon sources, which creates conditions similar to a 'microbial reactor' where substances are transformed and degraded through chemical and biological processes. The concrete corrosion in sewers is majorly caused by the presence of H_2S, and to a lesser extend CO_2, in the sewer gas in gravity sections of sewer transportation networks, pumping stations and sewage plants.

The occurrence of H_2S in the sewer gas is related to the metabolism of sulfate-reducing bacteria in anaerobic sections of sewers such as rising main sewers. Due to the low dissolved oxygen levels in wastewater, sulfate become the major electron donor, leading to the biological formation of hydrogen sulfide. During wastewater transportation, the sulfide generated can be either chemically or biological oxidized in wastewater, or partition into sewer gas due to changes in water pressure, turbulences, temperature and pH. The chemical or biological oxidation of sulfide in wastewater results in the formation of various oxidation products including elemental sulfur, thiosulfate, and sulfate. The partition of gaseous hydrogen sulfide from wastewater into sewer gas is highly pH-dependent although further factors such as turbulences, temperature, and sewer pipe design also play a role. The hydrogen sulfide in the sewer gas leads to chemically and microbiologically influenced concrete corrosion.

Intact concrete usually has a high pH of around 13, which is not suitable for the colonization of most microorganisms. The H_2S in sewer gas reacts with the alkaline concrete directly, leading to the dissolution of portlandite and corresponding pH reduction. While under extreme H_2S concentrations, H_2S can be chemically oxidized directly to sulfuric acid. These reactions reduce the surface pH of concrete, leading to microbiologically influenced concrete corrosion.

The microbiologically influenced concrete corrosion starts when sulfur-oxidizing microorganisms colonize concrete surfaces. Through the biological oxidation of H_2S, biologically produced sulfuric acid on concrete surfaces leads to the formation of corrosion products such as calcium sulfates (i.e., anhydrite, basanite, and gypsum), ettringite and amorphous silica. These corrosion products are of expansive nature, inducing micro- and macro cracking, while providing minimum structural strength and resulting in the mass loss. Very high concrete corrosion rates of > 1 cm/a will eventually lead to a failure of the affected concrete structures.

References

1. Apgar, P., Witherspoon, J.: Minimization of Odors and Corrosion in Collection Systems (2008)
2. Boon, A.G.: Septicity in sewers: causes, consequences and containment. Water Sci. Technol. **31,** 237–253 (1995)
3. Buisman, C., Uspeert, P., Janssen, A., Lettinga, G.: Kinetics of chemical and biological sulphide oxidation in aqueous solutions. Water Res. **24**, 667–671 (1990)
4. Carrera, L., Springer, F., Lipeme-Kouyi, G., Buffiere, P.: A review of sulfide emissions in sewer networks: overall approach and systemic modelling. Water Sci. Technol. **73**, 1231–1242 (2016)
5. Chen, K.Y., Morris, J.C.: Kinetics of oxidation of aqueous sulfide by oxygen. Environ. Sci. Technol. **6**, 529–537 (1972)
6. Chetty, K., Xie, S., Song, Y., McCarthy, T., Garbe, U., Li, X., Jiang, G.: Self-healing bioconcrete based on non-axenic granules: a potential solution for concrete wastewater infrastructure. J. Water Process Eng. **42**, 102139 (2021)
7. Gartner, E., Young, J., Damidot, D., Jawed, I.: Hydration of Portland cement. Struct. Perform. Cem. **13**, 978 (2002)
8. Grengg, C., Ukrainczyk, N., Koraimann, G., Mueller, B., Dietzel, M., Mittermayr, F.: Long-term in situ performance of geopolymer, calcium aluminate and Portland cement-based materials exposed to microbially induced acid corrosion. Cem. Concr. Res. **131**, 106034 (2020)
9. Houst, Y.F.: The role of moisture in the carbonation of cementitious materials. Int. Z. Bauinstandsetzen Baudenkmalpflege **2**, 49–66 (1996)
10. Hvitved-Jacobsen, T., Vollertsen, J., Matos, J.S.: The sewer as a bioreactor—a dry weather approach. Water Sci. Technol. **45**, 11–24 (2002)
11. Islander, R.L., Devinny, J.S., Mansfeld, F., Postyn, A., Shih, H.: Microbial ecology of crown corrosion in sewers. J. Environ. Eng. **117**, 751–770 (1991)
12. Jiang, G., Keller, J., Bond, P.L.: Determining the long-term effects of H_2S concentration, relative humidity and air temperature on concrete sewer corrosion. Water Res. **65**, 157–169 (2014)
13. Jiang, G., Keller, J., Bond, P.L., Yuan, Z.: Predicting concrete corrosion of sewers using artificial neural network. Water Res. **92**, 52–60 (2016)

14. Jiang, G., Sharma, K.R., Guisasola, A., Keller, J., Yuan, Z.: Sulfur transformation in rising main sewers receiving nitrate dosage. Water Res. **43**, 4430–4440 (2009)
15. Jiang, G., Sun, X., Keller, J., Bond, P.L.: Identification of controlling factors for the initiation of corrosion of fresh concrete sewers. Water Res. **80**, 30–40 (2015)
16. Jiang, G., Wightman, E., Donose, B.C., Yuan, Z., Bond, P.L., Keller, J.: The role of iron in sulfide induced corrosion of sewer concrete. Water Res. **49**, 166–174 (2014)
17. Joseph, A.P., Keller, J., Bustamante, H., Bond, P.L.: Surface neutralization and H_2S oxidation at early stages of sewer corrosion: influence of temperature, relative humidity and H_2S concentration. Water Res. **46**, 4235–4245 (2012)
18. Keller-Lehmann, B., Corrie, S., Ravn, R., Yuan, Z., Keller, J.: Preservation and simultaneous analysis of relevant soluble sulfur species in sewage samples. In: Proceedings of the Second International IWA Conference on Sewer Operation and Maintenance, p. 28. Citeseer (2006)
19. Kleinjan, W., de Keizer, A., Janssen, A.: Elemental sulfur and sulfur-rich compounds I. Top. Curr. Chem. **230**, 167–188 (2003)
20. Kulandaivelu, J., Choi, P.M., Shrestha, S., Li, X., Song, Y., Li, J., Sharma, K., Yuan, Z., Mueller, J.F., Wang, C., Jiang, G.: Assessing the removal of organic micropollutants from wastewater by discharging drinking water sludge to sewers. Water Res. **181**, 115945 (2020)
21. Kulandaivelu, J., Gao, J., Song, Y., Shrestha, S., Li, X., Li, J., Doederer, K., Keller, J., Yuan, Z., Mueller, J.F.: Removal of pharmaceuticals and illicit drugs from wastewater due to ferric dosing in sewers. Environ. Sci. Technol. (2019)
22. Li, X., Jiang, G., Kappler, U., Bond, P.: The ecology of acidophilic microorganisms in the corroding concrete sewer environment. Front. Microbiol. **8**, 683 (2017)
23. Li, X., Kulandaivelu, J., O'Moore, L., Wilkie, S., Hanzic, L., Bond, P.L., Yuan, Z., Jiang, G.: Synergistic effect on concrete corrosion control in sewer environment achieved by applying surface washing on calcium nitrite admixed concrete. Constr. Build. Mater. **302**, 124184 (2021)
24. Li, X., O'Moore, L., Song, Y., Bond, P.L., Yuan, Z., Wilkie, S., Hanzic, L., Jiang, G.: The rapid chemically induced corrosion of concrete sewers at high H_2S concentration. Water Res. **162**, 95–104 (2019)
25. Li, X., O'Moore, L., Wilkie, S., Song, Y., Wei, J., Bond, P.L., Yuan, Z., Hanzic, L., Jiang, G.: Nitrite admixed concrete for wastewater structures: mechanical properties, leaching behavior and biofilm development. Constr. Build. Mater. **233**, 117341 (2020)
26. Mehta, P.K.: Concrete. Structure, Properties and Materials (1986)
27. Millero, F.J., Hubinger, S., Fernandez, M., Garnett, S.: Oxidation of H_2S in seawater as a function of temperature, pH, and ionic strength. Environ. Sci. Technol. **21**, 439–443 (1987)
28. Mori, T., Nonaka, T., Tazaki, K., Koga, M., Hikosaka, Y., Noda, S.: Interactions of nutrients, moisture and pH on microbial corrosion of concrete sewer pipes. Water Res. **26**, 29–37 (1992)
29. Nica, D., Davis, J.L., Kirby, L., Zuo, G., Roberts, D.J.: Isolation and characterization of microorganisms involved in the biodeterioration of concrete in sewers. Int. Biodeterior. Biodegradation **46**, 61–68 (2000)
30. Nielsen, A.H., Hvitved-Jacobsen, T., Vollertsen, J.: Kinetics and stoichiometry of sulfide oxidation by sewer biofilms. Water Res. **39**, 4119–4125 (2005)
31. Nielsen, A.H., Vollertsen, J., Hvitved-Jacobsen, T.: Determination of kinetics and stoichiometry of chemical sulfide oxidation in wastewater of sewer networks. Environ. Sci. Technol. **37**, 3853–3858 (2003)
32. Nielsen, A.H., Vollertsen, J., Hvitved-Jacobsen, T.: Kinetics and stoichiometry of aerobic sulfide oxidation in wastewater from sewers—effects of pH and temperature. Water Environ. Res. **78**, 275–283 (2006)
33. Nielsen, A.H., Vollertsen, J., Jensen, H.S., Madsen, H.I., Hvitved-Jacobsen, T.: Aerobic and anaerobic transformations of sulfide in a sewer system—field study and model simulations. Water Environ. Res. **80**, 16–25 (2008)
34. Page, C.L., Page, M.M.: Durability of Concrete and Cement Composites. Elsevier (2007)
35. Parker, C.: The corrosion of concrete 2. The function of *Thiobacillus concretivorus* (nov. spec.) in the corrosion of concrete exposed to atmospheres containing hydrogen sulphide. Aust. J. Exp. Biol. Med. Sci. **23** (1945)

36. Pikaar, I., Rozendal, R., Yuan, Z., Keller, J., Rabaey, K.: Electrochemical Sulfide Abatement in Sewer Systems (2011)
37. Pikaar, I., Sharma, K.R., Hu, S., Gernjak, W., Keller, J., Yuan, Z.: Reducing sewer corrosion through integrated urban water management. Science **345**, 812–814 (2014)
38. Scrivener, K.L.: Backscattered electron imaging of cementitious microstructures: understanding and quantification. Cem. Concr. Compos. **26,** 935–945 (2004)
39. Song, Y., Chetty, K., Garbe, U., Wei, J., Bu, H., O'Moore, L., Li, X., Yuan, Z., McCarthy, T., Jiang, G.: A novel granular sludge-based and highly corrosion-resistant bio-concrete in sewers. Sci. Total Environ. **791**, 148270 (2021)
40. Song, Y., Tian, Y., Li, X., Wei, J., Zhang, H., Bond, P.L., Yuan, Z., Jiang, G.: Distinct microbially induced concrete corrosion at the tidal region of reinforced concrete sewers. Water Res. **150**, 392–402 (2019)
41. Sublette, K.L., Kolhatkar, R., Raterman, K.: Technological aspects of the microbial treatment of sulfide-rich wastewaters: a case study. Biodegradation **9**, 259–271 (1998)
42. Suzuki, I. (1999) Oxidation of inorganic sulfur compounds: chemical and enzymatic reactions. Can. J. Microbiol. **45,** 97–105
43. Taylor, H.F.W.: Cement Chemistry (1997)
44. Vollpracht, A., Lothenbach, B., Snellings, R., Haufe, J.: The pore solution of blended cements: a review. Mater. Struct. **49**, 3341–3367 (2016)
45. Wells, T., Melchers, R., Joseph, A., Bond, P., Vitanage, D., Bustamante, H., De Grazia, J., Kuen, T., Nazimek, J., Evans, T.: A collaborative investigation of the microbial corrosion of concrete sewer pipe in Australia. In: OzWater-12 Australia's National Water Conference and Exhibition, pp. 8–10, May, 2012
46. Wells, T., Melchers, R.E.: Modelling concrete deterioration in sewers using theory and field observations. Cem. Concr. Res. **77**, 82–96 (2015)
47. Zhang, L., de Schryver, P., de Gusseme, B., de Muynck, W., Boon, N., Verstraete, W.: Chemical and biological technologies for hydrogen sulfide emission control in sewer systems: a review. Water Res. **42**, 1–12 (2008)