



Mitigation of Microbially Influenced Corrosion of Concrete Sewers Using Nitrite

5

Xuan Li and Guangming Jiang

Abstract

Sewer systems are essential compartments of urban life, preventing human exposure to unhygienic sewage and sewage-borne diseases. However, microbially influenced concrete corrosion (MICC) occurs in sewers globally and ultimately leads to severe structural deterioration and early failure of those concrete structures. The MICC in sewers is mainly caused by hydrogen sulfide (H_2S) that occurs in the headspace gas. In sewers, H_2S is produced due to the metabolism of sulfate-reducing bacteria (SRB) under anaerobic conditions in parts of sewers and is subsequently released into headspace sewer gas in the gravity sections of the sewer system. In gravity sewers, H_2S in the headspace gas is further oxidized into sulfuric acid by sulfide-oxidizing microorganisms (SOMs) on concrete surfaces, leading to concrete corrosion. The remediation and replacement of corroding concrete sewers could cost billions of dollars annually, which becomes a huge financial burden worldwide. In recent years, advanced understanding of inhibitory and biocidal effects of nitrite or free nitrous acid (HNO_2 , FNA), the protonated form of nitrite, on microorganisms, has led to the development of a series of nitrite-based applications in the bioremediation of sewer corrosion. These applications target at (1) reducing H_2S production in anaerobic sewers, (2) mitigating the corrosion development of existing corroding sewers, and (3) implementing new concrete with nitrite admixture for long-term corrosion control with minimum maintenance. This chapter provides a comprehensive summary of the current status of nitrite-based applications in the remediation and control of concrete sewer corrosion.

X. Li · G. Jiang (✉)

School of Civil, Mining and Environmental Engineering, University of Wollongong, Wollongong, NSW, Australia

e-mail: gjiang@uow.edu.au

© The Author(s), under exclusive license to Springer Nature Singapore Pte Ltd. 2022

S. Arora et al. (eds.), *Biotechnological Innovations for Environmental Bioremediation*, https://doi.org/10.1007/978-981-16-9001-3_5

119

KeywordsSewer · Concrete · Corrosion · Nitrite · Free nitrous acid

5.1 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. To ensure the durability and reliability of sewer infrastructures, concrete is widely used in the construction due to its high compressive strength (Söylev and Richardson 2008). Typically, concrete structures in sewers are designed to perform for 50–100 years with minimal maintenance (Monteiro and Kurtis 2003). However, severe structural deterioration and early failure of sewers due to corrosion occur worldwide, which shortens the expectancy of sewer service life by more than 50% (Monteiro and Kurtis 2003). The remediation cost for sewer corrosion is estimated to reach over \$390 billion within the next 20 years in the USA (Gutiérrez-Padilla et al. 2010). Furthermore, sewer networks can be considered as a reactor where transformations of a broad range of chemicals occur through chemical and biological reactions. Some products from in-sewer chemical or biological processes, such as hydrogen sulfide (H_2S) and volatile organic sulfur compounds, are malodorous and harmful to human health. Concrete corrosion in sewers thereby increasingly triggers high economic expenses, as well as severe health and environmental concerns (Grengg et al. 2018).

Concrete corrosion is a complex process with various chemical and biological reactions between concrete and sewer gases (i.e., CO_2 and H_2S) in gravity sewers (Jiang et al. 2015). Hydrogen sulfide (H_2S), in particular, is ubiquitous in gravity sections of sewers. Through chemical and/or biological reactions, H_2S consumes the alkalinity of concrete pipes, producing loose corrosion products such as gypsum and ettringite that have poor structural capacity. The corrosion process leads to weakened structure and eventual collapse of the concrete (Li et al. 2017). Since the biological oxidation rate is much higher than the chemical oxidation rate, microbially influenced concrete corrosion (MICC) is regarded as the main cause of sewer concrete deterioration (Hvitved-Jacobsen et al. 2013).

Nitrite has been recently applied in the wastewater field as an inhibitor or biocidal agent for sewer corrosion control and bioremediation. Promising results have been achieved with the application of nitrite at different phases of sewers. This chapter provides an overview of the sewer system, and concrete corrosion process, and summarizes the current status of nitrite-based applications in the remediation and control of concrete sewer corrosion.

5.2 Sewer System and Concrete Corrosion

5.2.1 Sewer System

5.2.1.1 Overview of the Sewer System

The sewer system is mainly designed for wastewater collection and transportation among various wastewater infrastructures (Hvitved-Jacobsen et al. 2013). The applications of sewer systems prevent human exposure to unhygienic sewage and sewage-borne disease. The ancient sewers were built using brick and mortar. However, in modern society, concrete is considered a more cost-effective material and has been applied predominantly for constructing sewer pipes (Söylev and Richardson 2008). The total length of sewers in Australia is almost 117,000 km, and approximately 40% of this network is constructed of concrete (Cayford 2012). Based on the wastewater flow conditions, sewers can be further divided into rising mains and gravity flow regions (Fig. 5.1). The rising main sections are operated with no gas phase, pumping the wastewater to a higher altitude. Gravity regions are usually partially filled with wastewater and wastewater flows downstream due to gravity (Fig. 5.1). Buried deep beneath the ground, sewer pipes ideally serve for 50–100 years with minimal maintenance considering the property of concrete itself (Monteiro and Kurtis 2003).

With the broad range of pollutants and the high microbial presence in wastewater, sewers function as “microbial reactors” where substances are transformed and degraded through chemical and biological processes (Hvitved-Jacobsen et al. 2013). Sewer system contains five main components: wastewater, biofilms, sewer gas in gravity sewers, sewer sediments, and concrete sewer walls (Fig. 5.1). The concrete walls allow the development of biofilms and sediments, where most of the microbial processes occur. Wastewater and sewer air mainly provide the energy/nutrient source for these microbial processes (Hvitved-Jacobsen et al. 2013). In

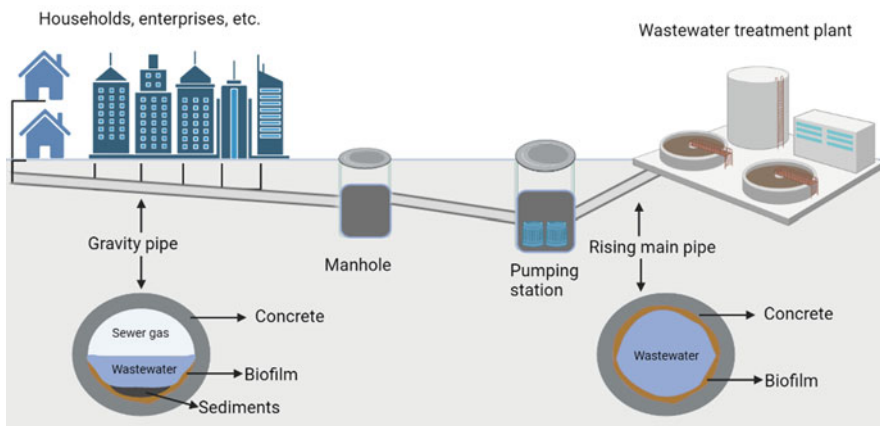
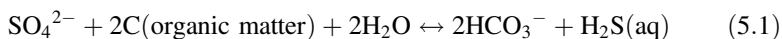


Fig. 5.1 An overview of the sewer system

sewers under anaerobic conditions, the H₂S and methane generations cause some main health concerns for sewer networks (Jiang et al. 2010; Lin et al. 2015). In partially filled gravity sewers, with the existence of both sewer air and wastewater, the microbial process can be complex. Due to the limitation of oxygen diffusion in anaerobic parts of the gravity sewer, sulfate may remain the main electron acceptor (Hvitved-Jacobsen et al. 2013). However, in aerobic parts, oxygen from the sewer air becomes the main electron acceptor, oxidizing H₂S in the sewer air (Okabe et al. 2007).

5.2.1.2 Sulfide in Sewers

Within the sewer system, the sulfur cycle is one of the most complex nutrient cycles. Various sulfur compounds exist and can be transformed into many oxidation states in wastewater through both biotic and abiotic processes (Suzuki 1999). Sulfate and sulfide are the most dominant species in wastewater with elemental sulfur present only as an intermediary or a product of highly localized conditions (Hvitved-Jacobsen et al. 2002). The concentration of dissolved sulfate is typically 20–200 mg/L in wastewater (Zhang et al. 2008). Underneath the wastewater, porous concrete pipes provide the habit for microorganisms (Hvitved-Jacobsen et al. 2002; Zhang et al. 2008). Due to the depletion of oxygen, the submerged areas become thermodynamically favorable for sulfate-reducing bacteria (SRB) to use sulfate as an electron acceptor for growth (Eq. (5.1)). Some SRB can also grow with sulfite or thiosulfate as electron acceptor (Hao et al. 1996). Hydrogen sulfide is thus produced by SRB, and this production is facilitated by high sulfate concentrations, low dissolved oxygen (DO), low flows, and long residence times (Ling 2013). The critical DO for sulfide production is below 0.5 mg/L; otherwise, SRB activity could be inhibited and sulfide can be chemically oxidized (Hao et al. 1996; Hvitved-Jacobsen et al. 2002).



The buildup and accumulation of sulfide in wastewater would finally lead to its emission into the sewer atmosphere in gravity sections of sewers (i.e., gravity pipes, wet wells, and manholes). Among the sulfide species, hydrogen sulfide is the only species that can partition into the sewer gas (Ling 2013). The partition process of H₂S is pH-dependent. The first and second dissociation of sulfide in aqueous solutions are described as Eq. (5.2) and Eq. (5.3), with pK_{a1} value of 7 and pK_{a2} ranging from 11.96 to 17.00 (Lens and Pol 2000). Lower wastewater pH could lead to more hydrogen sulfide emission (Hvitved-Jacobsen et al. 2002).



Aside from the sewage pH, other factors, such as higher sewage temperature and high turbulence intensity, can also promote the hydrogen sulfide emission from

wastewater (Carrera et al. 2015). Hydrogen sulfide is a highly toxic, irritant, and flammable gas with a characteristic smell of “rotten eggs” and is one of the main compounds of the odor in sewers (Jiang et al. 2017). Although there are volatile organic compound (VOC) emissions from the wastewater to the sewer gas, the concentrations are actually low at ppb to ppm levels or even less (Wu et al. 2006; Chan and Hanaeus 2006; Huang et al. 2012). The smell of sewer gas is mainly caused by H₂S, which comes with serious Occupational Health and Safety (OH&S) concerns to sewer workers and odor complaints from the community (Jiang et al. 2015). More importantly, the emission of H₂S also leads to the corrosion in gravity sewers, which significantly shortens the service life of sewer pipes (Jiang et al. 2016).

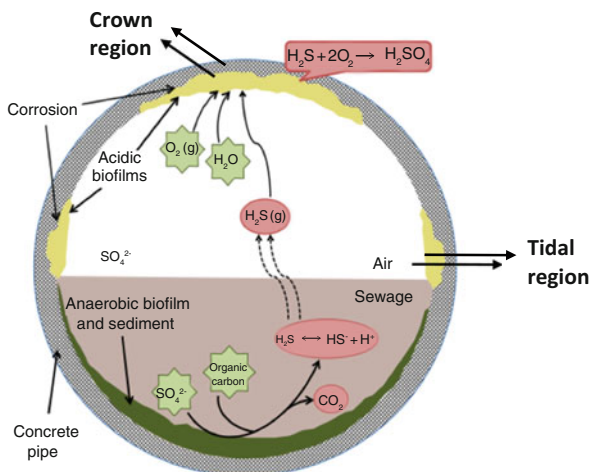
5.2.2 Concrete Corrosion in Sewers

5.2.2.1 Overview of Sewer Concrete Corrosion

H₂S in the gas phase is the precursor to corrosion in sewers. As discussed above, H₂S is generated in anaerobic sections of sewer pipe due to the metabolism of SRB and subsequently released into the headspace in gravity pipes, manholes, and pumping stations (Parker 1945; Jiang et al. 2015). This acidic gas could react with alkaline concrete pipes (pH > 13 for new concrete) and initiates the corrosion. The corrosion process initiates when the intact concrete with high pH (ca. 13) reacts with H₂S and CO₂ directly, lowering the pH to ca. 9 (Hvitved-Jacobsen 2001). Then sulfide-oxidizing microorganisms (SOMs) colonize on the concrete surface and further reduce the pH of concrete to below 3 (Sun et al. 2015). Once SOMs are well developed on concrete surfaces, MICC predominately contributes to the corrosion of concrete sewers (Li et al. 2020a). Depending on the surface pH, various SOMs have been detected in the corrosion layer. With pH ranging from 5 to 9, *Thiothrix* spp., *Thiobacillus plumbophilus* (formally as *Sulfuriferula plumbophilus*), *Thiomonas* sp., and *Halothiobacillus neapolitanus* have been detected (Okabe et al. 2007; Santo Domingo et al. 2011). *Thiothrix* spp. and *Thiomonas* spp. have the ability to grow chemoorganoheterotrophically or chemolithoautotrophically using either organic carbon or the inorganic sulfur species H₂S, S₂O₃²⁻, and S⁰ as electron donors. In comparison, *Halothiobacillus* sp. are obligate chemolithoautotrophic sulfur-oxidizing bacteria (Li et al. 2017). With pH lower than 5, acidophilic SOMs dominate the concrete surface, including *Acidithiobacillus* spp., *Acidiphilium* spp., *Mycobacterium* spp., and *Ferroplasma* spp. (Li et al. 2017). The sulfuric acid generated by SOMs reacts with the alkaline components of concrete, leading to the mass loss of concrete (Hvitved-Jacobsen 2001) (Fig. 5.2).

Both abiotic and biotic corrosion processes heavily depend on the water content of the concrete (Joseph et al. 2012; Ward et al. 2011; Wells et al. 2012). Within the sewer, concrete corrosion mostly occurs in the regions just above the sewage flow level and at the ceiling of the headspace, respectively, being referred to as the “tidal region” and the “crown region” (Fig. 5.2). The tidal regions are areas where the concrete of the sewer is frequently wetted by wastewater, while the crown regions

Fig. 5.2 A diagram of a cross section of a gravity concrete sewer pipe showing the major transformations occurring that lead to the acid formation in the upper aerobic biofilms and the onset of sewer corrosion, adapted from Li et al. (2017)



are exposed to the headspace of sewer gas and only very occasionally (during flooding) are in contact with the wastewater (Fig. 5.2). For crown regions, with high relative humidity (RH) (60–100%) in the sewer gas, moisture will condensate on the crown region, as the walls of sewer pipe usually have a lower temperature than the sewer atmosphere due to cooling from the surrounding soil (Joseph et al. 2012, Ward et al. 2011, Wells et al. 2012). In the tidal regions, sewer walls are frequently wetted by wastewater flooding, which will increase the water content of the concrete in those regions.

5.2.2.2 Corrosion Layer Conditions

Once the corrosion is well developed, on the corroding concrete surface, a soft (cottage cheese like) moist layer forms comprising largely of crystalline gypsum and other sulfur species (Cayford 2012). The microbial biofilms exist within the corrosion layer together with corrosion products (Fig. 5.3). Due to the paucity of nutrients innately present in concrete, the development of microorganisms mainly relies on the sewer gases and wastewater. The diffusion of gases (i.e., CO_2 , H_2S) provides volatile substrates and nutrients for the development of SOM (Jiang et al. 2014). And some exudates from microorganisms' metabolization and wastewater flooding (especially in tidal regions) can also be used as nutrients for the biofilms in corrosion layers (Nica et al. 2000).

The microbial biofilm is dense near the surface of the corrosion layer where the diffused oxygen and H_2S levels are high. Sulfuric acid is generated by SOM in the biofilm, and this diffuses through the corrosion layer toward the surface of the intact concrete (Okabe et al. 2007). With the acid diffusion, the gypsum ($\text{pH} < 3$) and ettringite zones ($\text{pH} > 3$) are formed and as they are expansive, together with iron mineral precipitation, cause cracking of the intact concrete (Fig. 5.3).

Corrosion significantly reduces the service life of sewers, which ultimately leads to severe structural deterioration and early failure of sewers. Since the pipes typically

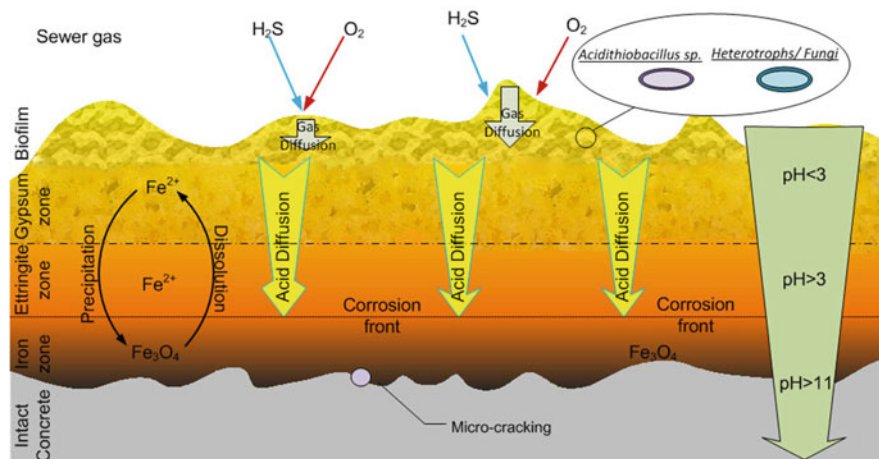


Fig. 5.3 A conceptual model for the sewer concrete corrosion layers (Li et al. 2017)

run below streets or developed property, sewer replacement and rehabilitation are difficult and cause a huge financial expenditure (Pikaar et al. 2014). Annual rehabilitation costs were estimated to reach over €450 million in Germany, £85 million in the UK, and over \$12 billion in the USA, respectively (Grengg et al. 2018). As occurrences and severity of corrosion are exacerbated in the coming years, much more expenditure is expected for the rehabilitation and control of concrete corrosion, which is a significant financial pressure on wastewater utilities and associated governmental agencies.

5.3 Applications of Nitrite in Sewer Systems

5.3.1 Reducing H₂S Production in Anaerobic Sewers

The antimicrobial effect of nitrite has been known for decades in the food industry. In the last decade, increasing evidence has shown that nitrite is inhibitory to the metabolism of a variety of key microorganisms in the wastewater system (Duan et al. 2020). In particular, strong biocidal or inhibitory effects have been observed with sewer biofilm, including critical micrograms for H₂S production (i.e., SRB). The sulfide control effect of nitrite was firstly tested through laboratory studies, where a continuous addition of nitrite at 20–140 mg-N/L for 25 days reduced the sulfide production by >90% (Table 5.1). The sulfide production ratio gradually reached the pre-addition condition after 2.5 months, suggesting a long-lasting effect of nitrite (Mohanakrishnan et al. 2008). Following this, the dependency of the inhibitory effect on nitrite levels and the exposure time was investigated with a range of nitrite concentrations (40, 80, 120 mg-N/L) and exposure time up to 24 days (Jiang et al. 2010). With continuous dosing of 80–120 mg-N/L of nitrite for 24 days, the sulfide

Table 5.1 A summary of dosage and results of nitrite or FNA dosing in reducing sulfide production in sewers

Chemicals	Condition	Dosage	Frequency	Reduction ratio	Recovery	Reference
Nitrite	Laboratory	20–140 mg-N/L	Continuous dosing for 25 days	>90%	2.5 month	Mohanakrishnan et al. (2008)
	Laboratory	40 mg-N/L	Continuous dosing for 24 days	About 80%	About 60 days	Jiang et al. (2010)
	Real sewer	80, 120 mg-N/L 100 mg-N/L	Continuous dosing for 3 days	>95% >90%	3 weeks	
FNA	Laboratory	0.26 mg-N/L	12 h/5 days	>80%	N/A ^a	Jiang et al. (2011a)
	Laboratory	1.54 mg-N·h/L	6–8 h/week	88%–99%	N/A	Nguyen and Marano (2016)
FNA + H ₂ O ₂	Real sewer	0.26 mg-N/L	8–24 h/10 days	>80%	N/A	Jiang et al. (2013)
		0.26 mgN/L FNA with 60 mg/L H ₂ O ₂	8–24 h/10 days	>80%	N/A	

N/A not applicable

production activity was inhibited by more than 95%, and the recovery took about 60 days to reach the pre-addition condition (Jiang et al. 2010). This lasting effectiveness was believed to be due to the decreased or suppressed growth of SRB in biofilms during the dosing period, and the recovery of these populations required 1–2 months (Jiang et al. 2010). However, a field investigation was carried with much shorter dosing period, where similar reduction of SRB activity was achieved in a real sewer at the city of Gold Coast, Australia (Table 5.1). 100 mg-N/L of nitrite was dosed continuously for 33 hours, where the sulfide production was completely suppressed during dosing and the recovery took about 3 weeks (Jiang et al. 2010). This relatively short dosing period suggests that the lasting sulfide control effect was likely due to a biocidal rather than an inhibitory effect.

A follow-up study further investigated the lasting sulfide control effects achieved by a short-term dosing of nitrite under different pH and nitrite concentrations. In this study, the viable fraction of microorganisms in the anaerobic sewer biofilm reduced by 65–75% after 6–24-h treatment with 0–120 mg-N/L nitrite under pH levels of 5–7, suggesting a strong biocidal effect achieved by nitrite (Jiang et al. 2011b) (Table 5.1). More importantly, the level of the biocidal effect showed a much stronger correlation with the free nitrous acid (FNA) concentration, which is well described by an exponential function, than with the nitrite concentration or with the pH level, suggesting that FNA is the actual biocidal agent (Jiang et al. 2011b). FNA (HNO_2) is the protonated form of nitrite, of which the concentration is determined by the nitrite concentration and pH as Eq. (5.4).

$$\text{FNA as } \text{HNO}_2\text{-N} = \text{NO}_2^- \text{-N} / (\text{Ka} \times 10^{\text{pH}}) \quad (5.4)$$

where Ka is the ionization constant of the nitrous acid, $\text{Ka} = e^{-\frac{2300}{(270+\tau(^{\circ}\text{C}))}}$.

This is a significant finding as it implies that the level of FNA can be controlled by adjusting either the nitrite concentration or the pH. It is important to note that, for the same nitrite concentration, the FNA concentration would increase by ten times when pH is lowered by one unit (Anthonisen et al. 1976). The strong biocidal effect of FNA leads to the possibility of intermittent dosing of FNA as a measure for controlling sulfide in sewers. For a successful application of intermittent dosing, three parameters, i.e., dosing concentration, exposure time (dosing duration), and the dosing interval (repetition frequency), are critical. A comprehensive evaluation of FNA concentration ranging from 0.18 to 0.36 mg-N/L, exposure time of 12–96 h, and a dosing interval of 4, 8, and 12 days was conducted under laboratory conditions (Jiang et al. 2011a). It was demonstrated that FNA as low as 0.26 mg-N/L was able to suppress sulfide production after an exposure of 12 h, and with a dosing interval of 5 days. The average sulfide production under such a dosing scheme was reduced by >80% (Table 5.1). This study demonstrated the feasibility and effectiveness of intermittent dosing, which is more economically applicable. Furthermore, the inactivation kinetic parameters of sewer biofilm by FNA were evaluated with a 2-fraction Bayesian model (Jiang and Yuan 2014). The study determined the most cost-effective dosage (FNA concentration times the exposure time) as 1.4 mg-N·h/L for the 80% control efficiency of hydrogen sulfide (Table 5.1).

The long-term effectiveness of FNA dosing for control of sulfide production was further tested in a full-scale rising main sewer located in the city of Gold Coast, Australia, for 6 months (Jiang et al. 2013). One single dose of FNA or FNA + H₂O₂ for 8–24 h reduced the sulfide production by 80% for 10 days, confirming the effectiveness of intermittent dosing of FNA or FNA + H₂O₂ (Table 5.1). Furthermore, no biofilm adaptation or resistance to FNA was observed during the 6-month trial. Instead, successive dosing achieved better control efficiency which was thought to be due to repetitive weakening of the biofilms, suggesting an additional benefit for a long-term application (Jiang and Yuan 2013).

Besides nitrite or FNA, different types of chemicals have been applied in sewers to prevent sulfide production, including oxygen, nitrate, ferric/ferrous salts, and magnesium hydroxide. Oxygen and nitrate have been added into sewers to oxidize sulfide chemically and/or biologically to reduce the sulfide concentration (Zhang et al. 2008). Ferric/ferrous salt dosing targets at precipitating with sulfide to insoluble metal sulfide, and ferric salts also inhibit sulfide production by sewer biofilms (Jiang et al. 2015). Magnesium hydroxide (Mg(OH)₂) elevates wastewater pH, typically to 8.5–9.0, and thus reduces the transfer of hydrogen sulfide from water to the sewer air as well as sulfide productions (Gutierrez et al. 2009). However, all these chemicals require continuous dosing to achieve effective control, resulting in large chemical consumption and cost. The general cost of chemical dosing using these chemicals is estimated to be 0.04–0.18 \$/m³-wastewater in sewers. In comparison to these chemicals, the cost of intermittent FNA or FNA + H₂O₂ dosing in sewers is much less at 0.01–0.03 \$/m³, confirming the intermittent FNA/nitrite dosing as a cost-effective and environmentally friendly strategy for sulfide control in sewers (Duan et al. 2020).

5.3.2 Mitigating the Corrosion Development of Existing Corroding Sewers

The bactericidal effect achieved by FNA (formed by nitrite under acidic conditions) on sewer biofilms provides a possibility of controlling the MICC development in corroding sewers. Once MICC is well established on concrete surfaces, the corrosion layer is under acidic conditions with a pH lower than 3 (Sect. 5.2). This acid corrosion surface provides a perfect condition for the formation of FNA. A recent laboratory investigation sprayed sodium nitrite solution on corroding concrete surfaces to achieve a surface FNA concentration of 100–1000 ppm (Table 5.2). After the spray, the H₂S uptake rate (SUR) of coupons reduced by 84–92%, with no obvious recovery for up to 12 months, suggesting a long-lasting effect in inhibiting the corrosion development (Sun et al. 2015). This was attributed to the biocidal effect of the FNA (free nitrous acid, the protonated form of nitrite (HNO₂)), which formed on the acid corrosion surface by the nitrite solution. The biocidal effect was also evident by the sharp decrease of viable cells and ATP level by 75% and more than 98%, respectively (Table 5.2).

Table 5.2 A summary of results for nitrite application on corroding concrete

Chemicals	Conditions	Dosage	Mitigation effect	Recovery	Reference
Nitrite	Corroding concrete surface in laboratory corrosion conditions	FNA concentration of 100–1000 ppm	SUR reduced by 84–92%	No recovery for up to 12 months	Sun et al. (2015)
Nitrite	A solution containing scraped corrosion layers (pH < 3)	15.2 mg HNO ₂ -N/L	Viable cells decreased by 75%, ATP reduced by >98%	No recovery for up to 700 h	
Nitrite	Corroding concrete surface exposed in a real sewer manhole	FNA concentration of 100–1000 ppm	SUR and sulfate concentration in the corrosion layer reduced by 30%, 6 months after the spray	15 months after the spray	Li et al. (2022)

In comparison to the laboratory conditions (i.e., controlled H₂S concentration, temperature, and relative humidity), environmental conditions in real sewers are generally more dynamic. To further validate the effectiveness of spraying nitrite on corrosion control of concrete, a follow-up study was conducted in a real sewer manhole at the city of Gold Coast, Australia (Li et al. 2022). Two types of concrete were exposed to the corrosive conditions within a sewer manhole for 21 months, while nitrite spray was conducted at the 6th month of the exposure. Due to the nitrite spray, both the sulfide uptake rate (SUR) of coupons and sulfate content in the corrosion layer reduced by about 30%, 6 months after the spray, demonstrating the corrosion mitigation effect of nitrite. However, the reduction of SUR and sulfate content in the corrosion layers became <10%, 15 months after the spray (Li et al. 2022). The application of nitrite on coupons inside the real sewers showed a faster recovery of SOMs activity compared to the laboratory. This could be attributed to the dynamic sewer conditions with a high range of fluctuation of H₂S concentration and temperature, and also the potential wash-off of nitrite on the corrosion surface. Thus, an annual application of nitrite on corroding surface was recommended.

Besides nitrite spray, to mitigate the MICC of corroding sewers, physical and chemical treatments have been applied by (1) reducing the biological sulfide-oxidizing activity through removing the corrosion layer by high-pressure washing (Nielsen et al. 2008), (2) increasing the surface pH and deactivating the sulfide-oxidizing bacteria by application of magnesium hydroxide (Sydney et al. 1996), and (3) surfacing coating using silver bearing zeolite, epoxy, or polymer fiber (Berndt 2011). The surface washing effect was found to be temporary with a quick recovery of SOMs activity within 30–40 days after surface washing in a real sewer (Nielsen et al. 2008). The application of magnesium hydroxide and surface coating both

require a surface preparation before the application, which raises operational difficulties. In contrast to these techniques, nitrite spray requires no surface preparation before application, and the environmental and health concerns are limited as nitrite is regularly used as a substrate for denitrifying organisms in wastewater systems (Li et al. 2020a).

5.3.3 Increasing the Corrosion Resistance of Nitrite Admixed Concrete

The inhibitory effect of nitrite on SOMs was demonstrated by spraying a nitrite solution on corroding concrete surfaces (Sect. 3.2). However, this approach requires a continuous reapplication of nitrite on concrete due to the recovery of SOMs activity. Thus, nitrite admixed concrete, which contains calcium nitrite as an admixture during casting, was proposed to achieve a long-lasting effect with minimum maintenance. In a real sewer manhole, the corrosion loss of nitrite admixed concrete was reduced by 30% constantly for 18 months, compared to that of concrete without the nitrite admixture (Li et al. 2020b). The sulfide uptake activity was also reduced by 30%, confirming an inhibitory effect of nitrite on SOMs. Next-generation sequencing (NGS) further revealed a negative correlation between the calcium nitrite admixture in concrete and the abundance of SOMs. This field study for the first time demonstrated that using nitrite admixed concrete is a promising strategy to mitigate the MICC in sewers.

On nitrite admixed concrete, surface washing showed a synergistic mitigation effect on MICC control (Li et al. 2021). Conventionally, surface washing was considered as a temporary mitigation approach on Ordinary Portland Cement (OPC) concrete where the sulfide-oxidizing activity reached the pre-washing level in 30–40 days and 60–140 days after surface washing in a real sewer and laboratory chambers, respectively (Nielsen et al. 2008; Sun et al. 2016). This is majorly attributed to the quick recovery/re-establishment of SOMs on OPC concrete surfaces (Nielsen et al. 2008, Sun et al. 2016). However, on nitrite admixed concrete, the synergetic effect of calcium nitrite admixture in concrete and one single wash could lead to about 45 and 58% reduction in corrosion loss for concrete with 1 and 4% of calcium nitrite admixture, respectively, in a real sewer manhole for 10 months (Li et al. 2021). This combined use of nitrite admixed concrete and surface washing further provide a long-lasting effect on MICC mitigation.

To provide long-lasting corrosion mitigation, various techniques have been applied to increase the corrosion resistance of concrete. Water to cementitious materials ratio (w/c) is the primary factor that controls the properties of concrete (Gutiérrez-Padilla et al. 2010). Generally, decreases in the water/cement ratio of concrete mixtures lead to improvement of the mechanical properties and durability of concrete (Roy et al. 2001). Chemical acid immersion tests showed that concrete with lower w/c had lower corrosion loss (Mehta 1986). However, in some studies, concrete with a high w/c ratio (up to 50%) also yielded less mass loss after immersion in sulfuric acid (Hewayde et al. 2007). Changing concrete mix design

through the addition of admixtures, alternate binders or alternate aggregate can also chemically improve corrosion resistance. Current admixtures mainly focus on changing the physiochemical properties of concrete, such as adding polymers to reduce the permeability of concrete (Vincke et al. 2002). Supplementary cementitious materials (SCMs), including silica fume (SF) and fly ash (FA), have been applied commercially to improve the mechanical properties and sustainability of concrete. SF, the by-product of ferrosilicon alloy production, is an ultrafine powder consisting of spherical silicon dioxide (SiO_2) particles. FA, generated by coal combustion, is another fine-particle residue that includes silicon dioxide (SiO_2) and calcium oxide (CaO). With the fine particles and the pozzolanic characteristic, SF and FA reduce the porosity of concrete which results in denser concrete microstructure, higher structure performance, and reduced sulfuric acid penetration into the core of the concrete (Roy et al. 2001). Replacing 30 and 5% of cement with FA and SF resulted in good resistance to Na_2SO_4 solution (Roy et al. 2001). However, the increased chemical resistance cannot guarantee its resistance to MICC. For instance, the addition of SF enhanced the concrete corrosion loss with *Thiobacillus* sp. (a type of SOMs) (Fisher et al. 2008).

Calcium aluminate cement (CAC) showed up to six times higher corrosion resistance than OPC-based concrete in sewers (Kiliswa 2016). Recent studies revealed that this higher corrosion resistance is attributed to the higher acid neutralization capacity, the formation of an aluminum hydroxide gel under acid attack, and the possible bacteriostatic effect due to the higher Al content (Grenng et al. 2018). Nevertheless, the use of CAC concrete was limited as CAC concrete was not resistant to highly acidic conditions (pH 1–2) (Herisson et al. 2014). Although several investigations have found a high acid resistance and potential antimicrobial properties in geopolymers, there is no record of research evaluating the performance of geopolymer concrete related to MICC environments (Grenng et al. 2018). Antibiotic-loaded fibers and biocides such as tungsten and triclosan showed inhibitory effects on the growth of SOMs under laboratory conditions; however, these chemicals are toxic to the environment (De Muynck et al. 2009).

In contrast, the application of nitrite admixed concrete is environmentally friendly and has no adverse effect on concrete mechanical properties. The 28-day compressive strength of calcium nitrite admixed concrete with four different dosages (i.e., 1–4% weight of the cement) meets the structural requirement (Li et al. 2020c). Negligible changes in the community of anaerobic sewer biofilm developed on concrete in wastewater were observed due to the nitrite admixture (Li et al. 2020c). The leaching of nitrite into the sewer environment from the nitrite admixed concrete was slow, leading to a fairly low concentration of nitrite (ppb level) in wastewater (Li et al. 2020c). Furthermore, nitrite is regularly used as a substrate for denitrifying organisms in wastewater systems. Thus, the leached nitrite can be easily degraded within the sewer, which limits if any environmental and health concerns. Therefore, the addition of calcium nitrite into concrete is environmentally friendly to wastewater infrastructures with promising MICC mitigation effects.

References

- Anthonisen A, Loehr R, Prakasam T, Srinath E (1976) Inhibition of nitrification by ammonia and nitrous acid. *J Water Pollut Control Fed* 48:835–852
- Berndt M (2011) Evaluation of coatings, mortars and mix design for protection of concrete against sulphur oxidising bacteria. *Constr Build Mater* 25:3893–3902
- Carrera L, Springer F, Lipeme-Kouyi G, Buffiere P (2015) A review of sulfide emissions in sewer networks: overall approach and systemic modelling. *Water Sci Technol* 73:1231–1242
- Cayford BI (2012) Investigation of the microbial community and processes responsible for the corrosion of concrete in sewer systems. The degree of Doctor of Philosophy, University of Queensland
- Chan AA, Hanaeus J (2006) Odorous wastewater emissions, Vatten. *Cilt* 62:227
- De Muynck W, De Belie N, Verstraete W (2009) Effectiveness of admixtures, surface treatments and antimicrobial compounds against biogenic sulfuric acid corrosion of concrete. *Cem Concr Compos* 31:163–170
- Duan H, Gao S, Li X, Ab Hamid NH, Jiang G, Zheng M, Bai X, Bond PL, Lu X, Chislett MM, Hu S, Ye L, Yuan Z (2020) Improving wastewater management using free nitrous acid (FNA). *Water Res* 171:115382
- Fisher M, Bar-Nes G, Zeiri Y, Sivan A (2008) The effect of silica fume on biodegradation of cement paste and its capacity to immobilize strontium during exposure to microbial sulfur oxidation. *Biodegradation* 19:321–328
- Grengg C, Mittermayr F, Ukrainczyk N, Koraimann G, Kienesberger S, Dietzel M (2018) Advances in concrete materials for sewer systems affected by microbial induced concrete corrosion: a review. *Water Res* 134:341–352
- Gutierrez O, Park D, Sharma KR, Yuan Z (2009) Effects of long-term pH elevation on the sulfate-reducing and methanogenic activities of anaerobic sewer biofilms. *Water Res* 43:2549–2557
- Gutiérrez-Padilla MGD, Bielefeldt A, Ovtchinnikov S, Hernandez M, Silverstein J (2010) Biogenic sulfuric acid attack on different types of commercially produced concrete sewer pipes. *Cem Concr Res* 40:293–301
- Hao OJ, Chen JM, Huang L, Buglass RL (1996) Sulfate-reducing bacteria. *Crit Rev Environ Sci Technol* 26:155–187
- Herisson J, Guéguen-Minerbe M, Van Hullebusch ED, Chaussadent T (2014) Behaviour of different cementitious material formulations in sewer networks. *Water Sci Technol* 69:1502–1508
- Hewayde E, Nehdi M, Allouche E, Nakhla G (2007) Effect of mixture design parameters and wetting-drying cycles on resistance of concrete to sulfuric acid attack. *J Mater Civil Eng* 19:155–163
- Huang C-H, Chen K-S, Wang H-K (2012) Measurements and PCA/APCS analyses of volatile organic compounds in Kaohsiung municipal sewer systems, southern Taiwan. *Aerosol Air Qual Res* 12:1315–1326
- Hvitved-Jacobsen T (2001) Sewer processes: microbial and chemical process engineering of sewer networks. CRC Press, Boca Raton
- Hvitved-Jacobsen T, Vollertsen J, Matos JS (2002) The sewer as a bioreactor—a dry weather approach. *Water Sci Technol* 45:11–24
- Hvitved-Jacobsen T, Vollertsen J, Nielsen AH (2013) Sewer processes: microbial and chemical process engineering of sewer networks. CRC Press, Boca Raton
- Jiang G, Yuan Z (2013) Synergistic inactivation of anaerobic wastewater biofilm by free nitrous acid and hydrogen peroxide. *J Hazard Mater* 250:91–98
- Jiang G, Yuan Z (2014) Inactivation kinetics of anaerobic wastewater biofilms by free nitrous acid. *Appl Microbiol Biotechnol* 98:1367–1376
- Jiang G, Gutierrez O, Sharma KR, Yuan Z (2010) Effects of nitrite concentration and exposure time on sulfide and methane production in sewer systems. *Water Res* 44:4241–4251

- Jiang G, Gutierrez O, Sharma KR, Keller J, Yuan Z (2011a) Optimization of intermittent, simultaneous dosage of nitrite and hydrochloric acid to control sulfide and methane productions in sewers. *Water Res* 45:6163–6172
- Jiang G, Gutierrez O, Yuan Z (2011b) The strong biocidal effect of free nitrous acid on anaerobic sewer biofilms. *Water Res* 45:3735–3743
- Jiang G, Keating A, Corrie S, O'Halloran K, Nguyen L, Yuan Z (2013) Dosing free nitrous acid for sulfide control in sewers: results of field trials in Australia. *Water Res* 47:4331–4339
- Jiang G, Keller J, Bond PL (2014) Determining the long-term effects of H₂S concentration, relative humidity and air temperature on concrete sewer corrosion. *Water Res* 65:157–169
- Jiang G, Sun J, Sharma KR, Yuan Z (2015) Corrosion and odor management in sewer systems. *Curr Opin Biotechnol* 33:192–197
- Jiang G, Keller J, Bond PL, Yuan Z (2016) Predicting concrete corrosion of sewers using artificial neural network. *Water Res* 92:52–60
- Jiang G, Melder D, Keller J, Yuan Z (2017) Odor emissions from domestic wastewater: a review. *Crit Rev Environ Sci Technol* 47:1581–1611
- Joseph AP, Keller J, Bustamante H, Bond PL (2012) Surface neutralization and H₂S oxidation at early stages of sewer corrosion: influence of temperature, relative humidity and H₂S concentration. *Water Res* 46:4235–4245
- Kiliswa MW (2016) Composition and microstructure of concrete mixtures subjected to biogenic acid corrosion and their role in corrosion prediction of concrete outfall sewers. Thesis.
- Lens P, Pol LH (2000) Environmental technologies to treat sulfur pollution. IWA Publishing, London
- Li X, Kappler U, Jiang G, Bond PL (2017) The ecology of acidophilic microorganisms in the corroding concrete sewer environment. *Front Microbiol* 8:683
- Li X, Bond P, O'Moore L, Wilkie S, Hanzic L, Johnson I, Mueller K, Yuan Z, Jiang G (2020a) Increased resistance of nitrite-admixed concrete to microbially induced corrosion in real sewers. *Environ Sci Technol* 54:4
- Li X, Bond PL, O'Moore L, Wilkie S, Hanzic L, Johnson I, Mueller K, Yuan Z, Jiang G (2020b) Increased resistance of nitrite-admixed concrete to microbially induced corrosion in real sewers. *Environ Sci Technol* 54:2323–2333
- Li X, O'Moore L, Wilkie S, Song Y, Wei J, Bond PL, Yuan Z, Hanzic L, Jiang G (2020c) Nitrite admixed concrete for wastewater structures: mechanical properties, leaching behavior and biofilm development. *Construct Build Mater* 233:117341
- Li X, Kulandaivelu J, O'Moore L, Wilkie S, Hanzic L, Bond PL, Yuan Z, Jiang G (2021) Synergistic effect on concrete corrosion control in sewer environment achieved by applying surface washing on calcium nitrite admixed concrete. *Construct Build Mater* 302:124184
- Li X, Johnson I, Mueller K, Wilkie S, Hanzic L, Bond PL, O'Moore L, Yuan Z, Jiang G (2022) Corrosion mitigation by nitrite spray on corroded concrete in a real sewer system. *Sci Total Environ* 806:151328
- Lin H-W, Rabaey K, Keller JR, Yuan Z, Pikaar I (2015) Scaling-free electrochemical production of caustic and oxygen for sulfide control in sewers. *Environ Sci Technol* 49:11395–11402
- Ling AL (2013) Characterization and control of microbially induced concrete corrosion. The degree of Doctor of Philosophy, University of Colorado at Boulder
- Mehta PK (1986) Concrete. Structure, properties and materials. Prentice-Hall, Englewood Cliffs
- Mohanakrishnan J, Gutierrez O, Meyer RL, Yuan Z (2008) Nitrite effectively inhibits sulfide and methane production in a laboratory scale sewer reactor. *Water Res* 42:3961–3971
- Monteiro PJ, Kurtis KE (2003) Time to failure for concrete exposed to severe sulfate attack. *Cem Concr Res* 33:987–993
- Nguyen L, Marano V (2016) The Cloevis® biofilm removal system: results from early US commercial applications. *Proc Water Environ Fed* 2016(4):431–444
- Nica D, Davis JL, Kirby L, Zuo G, Roberts DJ (2000) Isolation and characterization of microorganisms involved in the biodeterioration of concrete in sewers. *Int Biodeterior Biodegrad* 46:61–68

- Nielsen AH, Vollertsen J, Jensen HS, Wium-Andersen T, Hvitved-Jacobsen T (2008) Influence of pipe material and surfaces on sulfide related odor and corrosion in sewers. *Water Res* 42:4206–4214
- Okabe S, Odagiri M, Ito T, Satoh H (2007) Succession of sulfur-oxidizing bacteria in the microbial community on corroding concrete in sewer systems. *Appl Environ Microbiol* 73:971–980
- Parker CD (1945) The corrosion of concrete. *Aust J Exp Biol Med Sci* 23:81–90
- Pikaar I, Sharma KR, Hu S, Gernjak W, Keller J, Yuan Z (2014) Reducing sewer corrosion through integrated urban water management. *Science* 345:812–814
- Roy D, Arjunan P, Silsbee M (2001) Effect of silica fume, metakaolin, and low-calcium fly ash on chemical resistance of concrete. *Cem Concr Res* 31:1809–1813
- Santo Domingo JW, Revetta RP, Iker B, Gomez-Alvarez V, Garcia J, Sullivan J, Weast J (2011) Molecular survey of concrete sewer biofilm microbial communities. *Biofouling* 27:993–1001
- Söylev TA, Richardson M (2008) Corrosion inhibitors for steel in concrete: state of the art report. *Construct Build Mater* 22:609–622
- Sun X, Jiang G, Bond PL, Keller J, Yuan Z (2015) A novel and simple treatment for control of sulfide induced sewer concrete corrosion using free nitrous acid. *Water Res* 70:279–287
- Sun X, Jiang G, Chiu TH, Zhou M, Keller J, Bond PL (2016) Effects of surface washing on the mitigation of concrete corrosion under sewer conditions. *Cem Concr Compos* 68:88–95
- Suzuki I (1999) Oxidation of inorganic sulfur compounds: chemical and enzymatic reactions. *Can J Microbiol* 45:97–105
- Sydney R, Esfandi E, Surapaneni S (1996) Control concrete sewer corrosion via the crown spray process. *Water Environ Res* 68:338–347
- Vincke E, Van Wanseele E, Monteny J, Beeldens A, De Belie N, Taerwe L, Van Gemert D, Verstraete W (2002) Influence of polymer addition on biogenic sulfuric acid attack of concrete. *Int Biodeterior Biodegrad* 49:283–292
- Ward M, Corsi R, Morton R, Knapp T, Apgar D, Quigley C, Easter C, Witherspoon J, Pramanik A, Parker W (2011) Characterization of natural ventilation in wastewater collection systems. *Water Environ Res* 83:265–273
- Wells T, Melchers R, Joseph A, Bond P, Vitanage D, Bustamante H, De Grazia J, Kuen T, Nazimek J, Evans T (2012) A collaborative investigation of the microbial corrosion of concrete sewer pipe in Australia. In: *Ozwater'12: Australia's national water conference and exhibition. Ozwater'12 Conference Proceedings* (Sydney, NSW 08-10 May, 2012), pp 1–8
- Wu B-Z, Feng T-Z, Sree U, Chiu K-H, Lo J-G (2006) Sampling and analysis of volatile organics emitted from wastewater treatment plant and drain system of an industrial science park. *Anal Chim Acta* 576:100–111
- Zhang L, De Schryver P, De Gussem B, De Muynck W, Boon N, Verstraete W (2008) Chemical and biological technologies for hydrogen sulfide emission control in sewer systems: a review. *Water Res* 42:1–12



Xuan Li obtained her Ph.D. at The University of Queensland, focusing on the corrosion mitigation for concrete sewers. She currently works as an associate research fellow at the University of Wollongong. She has a broad research interests in wastewater system management, concrete corrosion, microbiology, wastewater-based epidemiology, and artificial intelligence. Email: xuanl@uow.edu.au



Guangming Jiang was awarded his Ph.D. at The University of Queensland. He is an associate professor in the School of Civil, Mining and Environmental Engineering of the University of Wollongong, Australia. His research fields include wastewater treatment, environmental health, microbial corrosion, and smart water systems. Email: gjiang@uow.edu.au