Biodeterioration of Concrete Sewer Pipes: State of the Art and Research Needs

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Abstract: Biodeterioration of concrete sewers is a common problem that results in concrete disintegration and significant damage. Two stages are normally identifiable in the process: an initiation stage, during which the concrete pore water pH is reduced from an initial value of over 12 to a value of about 9 by ingress of hydrogen sulfide gas and carbon dioxide (carbonation) and subsequent reaction with the hydrated cement paste; and a second stage, active biodeterioration, during which microorganisms excrete sulfuric acid that attacks the hydrated cement paste (HCP). Various national codes and standards provide some guidance to mitigate this problem. Sulfur-oxidizing microorganisms growing on the sewer walls have been isolated as the main culprit, but other phenomena come into play before biodeterioration occurs. Steady-state biodeterioration rates of 3 mm/year have been proposed in the literature. A detailed literature review was conducted to evaluate the various aspects of concrete biodeterioration and determine further research needs. This state-of-the-art report summarizes the deterioration mechanisms involved in biodeterioration of concrete sewers and the work necessary to complete the modeling of this phenomenon. A conceptual model of the processes is presented. **DOI: 10.1061/(ASCE)PS.1949-1204.0000072.** *© 2011 American Society of Civil Engineers.*

CE Database subject headings: Biological processes; Concrete pipes; Gravity sewers; Sulfides; Carbonation; Deterioration; Turbulent flow; Research.

Author keywords: Biodegradation; Concrete; Gravity sewers; Carbonation; Deterioration mechanisms; Sulfides; Turbulent flow.

Introduction

Biodeterioration is the disintegration of a material caused by the actions of various living organisms which can vary widely, from marine borers (including mollusks and crustaceans) to insects, fungi, prokaryotes (including *Bacteria* and *Archea*), plants, and trees (Sanchez-Silva and Rosowsky 2008). The most prominent example of biodeterioration is the disintegration of materials caused by biogenic sulfuric acid produced in sewers. Sulfuric acid attacks most materials, and concrete is particularly sensitive because of its alkalinity. Its omnipresence in sewers makes it important in the study of biodeterioration mechanisms. The progressive deterioration of concrete sewer pipes normally occurs in two stages (Fig. 1):

- Stage 1: Initiation, chemical pH reduction. This stage is completely abiotic; the alkalinity of the concrete protects it from microbial growth, and therefore from biodeterioration. However, reactions with weak acids from the dissolution of gases present in the sewer atmosphere, such as carbonic acid (from carbon dioxide, CO_2; i.e., carbonation reaction) and hydrogen sulfide (from $H_2S_{(gas)}$, emitted from the sewage stream), consume the concrete alkalinity and reduce the surface pH. This stage ends when concrete pH reaches a value of about 9.

- Stage 2: Active biodeterioration. This stage is biotic; biofilms start to form on the concrete surface when pH is about 9. Hydrogen sulfide gas ($H_2S_{(gas)}$) is oxidized both chemically and by sulfur-oxidizing microorganisms (SOM); pH of the hydrated cement paste (HCP) continues to decrease until *Acidithiobacillus thiooxydans* grows in the biofilm and excretes sulfuric acid. At pH below 1, sulfuric acid production becomes self-inhibitory and the population of *A. thiooxydans* starts to decline. The HCP is transformed to gypsum and silicon dioxide as it reacts with the acid. The cementing properties of the matrix are lost, aggregates pop-out and the thickness of the concrete pipe decreases.

Biodeterioration is occasionally referred to as microbially induced corrosion of concrete (MICC) or microbial corrosion. Here, only the terms biodeterioration and deterioration will be used, because corrosion more commonly refers to deterioration by oxidoreduction of metallic components such as steel bars in concrete.

Biodeterioration occurs in unsubmerged sections of sewer pipes in contact with the air; pressure pipes are usually not affected. The wastewater must have conditions appropriate for the formation of sulfide and emission of hydrogen sulfide gas to the sewer atmosphere. In a gravity sewer system, shallow slopes with low oxygen penetration stimulate the formation of sulfides. Steep slopes causing turbulence increase the rate of release of $H_2S_{(gas)}$ in the sewer atmosphere (EPA 1992). Ideal conditions for biodeterioration are a section with a shallow slope and a long residence time, followed by a section with high turbulence. Biodeterioration will normally occur in the section with high turbulence.

Buried pipes subjected to external earth and live loads have the highest flexural (bending) tensile stresses in the concrete wall at the external side of the neutral axis at the springline, and on the internal side of the neutral axis at the crown and invert. The highest

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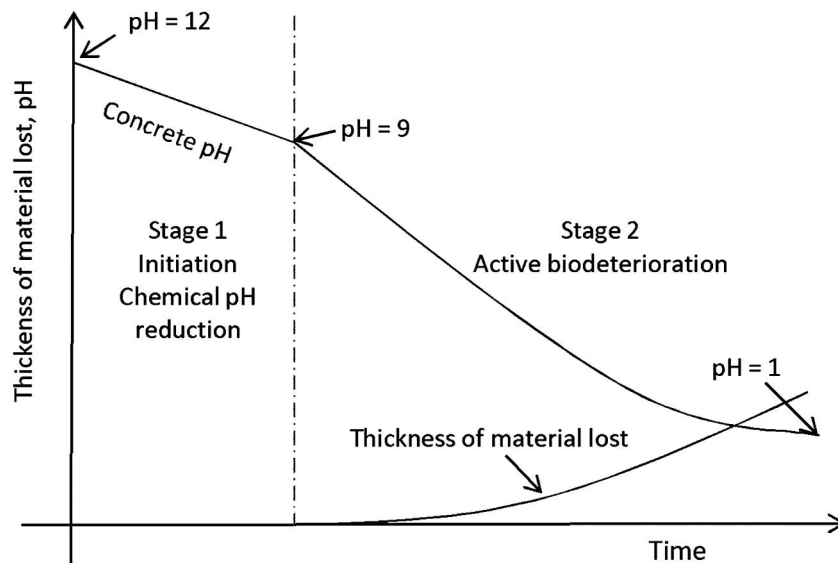J. Pipeline Syst. Eng. Pract., 2011, 2(2): 42-52

Fig. 1. Stages of biodeterioration (reprinted from Bastidas-Arteaga et al. 2008, with permission from Elsevier)

deterioration at the crown could be related to the cracking at that location; this would increase the surface area available for colonization by microorganisms and facilitate the ingress of deleterious substances when compared with other uncracked locations. At the water line, the highest availability of nutrients from splashing of sewage can be the cause of enhanced deterioration. At the invert, the concrete is protected from any biological deterioration, because it is always covered by wastewater and deleterious acids do not accumulate to high concentrations.

This state-of-the-art paper summarizes the important processes in biodeterioration of concrete sewer pipes; these include chemical reactions between the concrete and the various deleterious substances, characterization of the microorganisms involved, and modeling of the microbial processes. An understanding of these phenomena will facilitate the prediction of biodeterioration rates of concrete sewer pipes under different flow conditions and wastewater compositions.

Codes and Standards

Biodeterioration has received limited coverage in the various national codes and standards. The two main standards that deal with this deterioration phenomenon directly are summarized as follows.

In chapter 4 of American Concrete Institute (ACI) 350-06 (ACI 2006), durability requirements of concrete mixtures are prescribed based on exposure conditions; parameters such as the maximum water/cement ratios (w/c ratios), the minimum cement contents, and the minimum compressive strengths are defined here. The deleterious effects of sulfuric acid are treated separately from chemical or sulfate attacks, and are recognized as causes of the rapid deterioration of concrete. For structures subjected to such aggressive environments, secondary coatings or liners are recommended (ACI 2006).

The *Durable Concrete Structures Bulletin d'information No. 182* (Comité Euro-International du Béton 1989) defines biodeterioration as the mechanical or chemical effects of biological processes on concrete. Mechanical deterioration of the material refers to the physical growth of various organisms (e.g., tree root intrusion on a concrete sewer pipe), while chemical deterioration refers to changes in the material microstructure caused by excretion of

substances by microorganisms. Maximum water/cement ratio and minimum cement content of concrete mixtures used in sewers are dictated as they are exposed to highly aggressive chemical environments. Additional protective measures are prescribed to achieve proper durability. To reduce the risks of biodeterioration of concrete sewers, the design guide recommends reducing turbulence in sewers to limit the emission of hydrogen sulfide, removing the growth of sulfur-oxidizing microorganisms on the sewer walls, or ventilating the system so that hydrogen sulfide emitted from the sewage is rapidly flushed out of the sewer line (Comité Euro-International du Béton 1989).

Chemical Reactions with Concrete

Carbonation and hydrogen sulfide ingress occur during the initiation stage, prior to microbial colonization. The attacks of sulfuric acid and other organic acid occur during the active biodeterioration stage. Fig. 2 summarizes the various deleterious chemical reactions.

Carbonation

Carbonation is the ingress of gaseous carbon dioxide (CO_2) and its effects on concrete. Carbon dioxide combines with the water present in the hydrated cement paste pores to form carbonic acid [H_2CO_3, Eq. (1)]. Two steps can be identified: at first, calcium hydroxide dissolves and combines with carbonic acid to form calcium carbonate [Eq. (2)]; and then, carbonic acid reacts with other hydration products [C-S-H and C-A-H, Eqs. (3) and (4)] (Cerny and Rovnanikova 2002). The resulting reaction products form the carbonated layer; they are more voluminous than the initial compounds reducing the pore size of the HCP. Fully carbonated concrete has a pH of about 8. The carbonated layer impedes ingress of additional carbon dioxide; this layer can be a millimeter or less in thickness (Richardson 2002).

$$H_2O + CO_2 \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^- \rightarrow 2H^+ + CO_3^{2-} \quad (1)$$
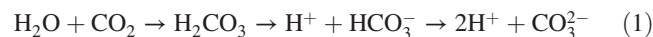
Water + carbon dioxide → carbonic acid → dissociated carbonic acid

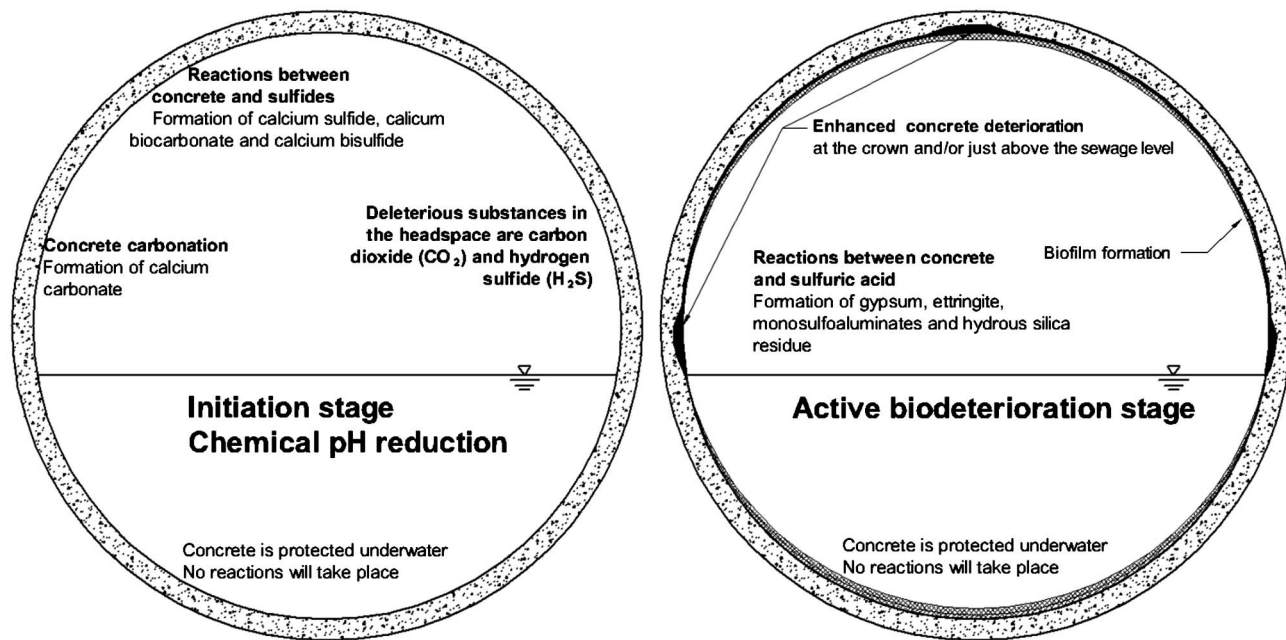$$Ca(OH)_2 + H_2CO_3 \rightarrow CaCO_3 + H_2O \quad (2)$$

Fig. 2. Chemical reactions between concrete and deleterious substances during biodeterioration (not to scale); biofilm thickness has been exaggerated to show processes

(First step)   Calcium hydroxide + carbonic acid → calcium carbonate + water

$$CaO.SiO_2.zH_2O + H_2CO_3 \rightarrow CaCO_3 + SiO_2.(z+1)H_2O \quad (3)$$

(Second step)   Calcium silicate hydrate + carbonic acid → calcium carbonate + hydrated silicon dioxide

$$kCaO.Al_2O_3.zH_2O + H_2CO_3 \rightarrow CaCO_3 + 2Al(OH)_3$$
$$+ (z-2)H_2O \quad (4)$$
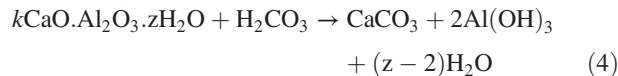
(Second step)   Calcium aluminate hydrate + carbonic acid → calcium carbonate + aluminum hydroxide + water

Hydrogen Sulfide

$H_2S_{(gas)}$ also reacts with the HCP phase of the concrete. Hydrogen sulfide dissociates in the same manner as carbonic acid [Eq. (5)]; pH reduction reactions are similar since both acids have two protons ($2H^+$). Calcium hydroxide is transformed to calcium sulfide when it comes in contact with hydrogen sulfide [Eq. (6)]. The carbonated layer can also be attacked as calcium carbonate reacts to form calcium sulfide and disulfide [Eqs. (7) and (8)] (Cerny and Rovnanikova 2002).
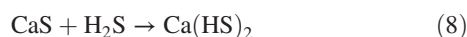
$$H_2S \rightarrow H^+ + HS^- \rightarrow 2H^+ + S^{2-} \quad (5)$$

Hydrogen sulfide → hydrogen ions + dissociated sulfide

$$Ca(OH)_2 + H_2S \rightarrow CaS + 2H_2O \quad (6)$$

Calcium hydroxide + hydrogen sulfide → Calcium sulfide + water

$$2CaCO_3 + H_2S \rightarrow Ca(HCO_3)_2 + CaS \quad (7)$$

Calcium carbonate + hydrogen sulfide → Calcium bicarbonate + Calcium sulfide

$$CaS + H_2S \rightarrow Ca(HS)_2 \quad (8)$$

Calcium sulfide + hydrogen sulfide → Calcium disulfide

Roberts et al. (2002) experimentally reproduced a reduction in pore water pH by exposing fresh concrete samples to hydrogen sulfide gas concentrations of 50, 100, and 250 ppm; carbon dioxide concentration was atmospheric (usually 380 ppm). The pH reduction is shown in Fig. 3 and given by

$$4.4 \times 10^{-5} \text{ pH unit/day/ppm of } H_2S$$
$$\times \text{ Concentration of } H_2S \text{ (ppm)} + 0.021 \text{ pH unit/day} \quad (9)$$

The pH decrease with a null concentration of hydrogen sulfide (0.021 pH unit/day) is probably caused by carbonation of the concrete, but the authors did not mention this.

The pH reduction rate for mortar coupons placed in sewers with $H_2S_{(gas)}$ concentration of 30 ppm $\pm$ 20 ppm for a period of 56 days was 0.06 pH unit/day; carbon dioxide concentration was not calculated (Okabe et al. 2007). Using Fig. 3, the expected pH reduction rate is 0.022 pH unit/day, approximately one-third of the observed rate. Both reduction rates are of the same order of magnitude and appear to be purely chemical.

However, Okabe et al. (2007) calculated a pH reduction rate of 0.013 pH unit/day from the rate of reduction attributable to H_2S in Eq. (9). This is 4.6 times higher than the rate previously observed and led Okabe et al. (2007) to conclude that microbial processes are involved in the first stage. However, the increase is only 2.7 times greater. Since the carbon dioxide concentrations were not monitored, it could explain the discrepancy between the observed and calculated rates. Variations between the experiments can also cause differences in the results:
- Roberts et al.: 50 to 250 ppm H_2S, fresh concrete samples, in the laboratory;
- Okabe experiment: 30 ppm H_2S, mortar samples, in situ.

Acids, Including Organic Acids

Acids will initially react with the concrete cover because of its alkaline-rich character (pH > 12), with the rate of attack being dependent primarily on the strength and pH of the acid and the solubility of the salts formed (Zivica and Bajza 2001). These salts can be eroded by flowing water (e.g., rain, streaming flow) or
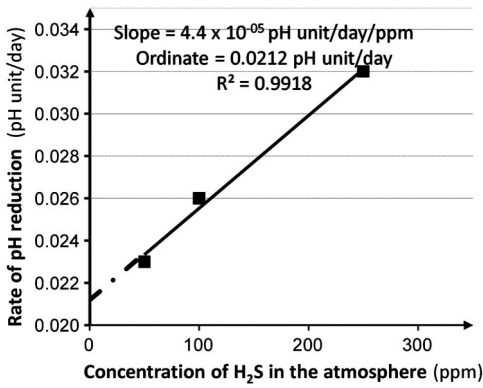
Fig. 3. Chemical surface pH reduction of fresh portland cement caused by hydrogen sulfide gas exposure (reprinted from Roberts et al. 2002, with permission from Elsevier)

blowing wind (with or without solid particles), exposing new surface to acid attack. However, if a protective layer is formed on the concrete surface, the rate of acid ingress and the resulting attack on the remaining concrete is determined by its permeability (ease with which the aggressive fluids can ingress into the remaining concrete). In addition, the ability of a concrete pipe or a cement mortar-lined pipe to maintain a pacifying, alkaline-rich environment (pH > 12) for the steel reinforcement, is directly related to the aggressiveness of the effluent and the reserve of alkaline-rich concrete constituents, such as the cement and limestone aggregates (if any). The principal HCP compounds and their stable pH values are (Beddoe and Dorner 2005; Pavlik 1994):

- Calcium hydroxide, 12.6;
- Ettringite, 10.7;
- C-S-H, 10.5;
- Calcium aluminates, below 10.5;
- Aluminum hydroxides, 4;

- Hydrated aluminum oxides, 3;
- Ferric hydroxides, 2; and
- Hydrous silica gel residue, less than 2.

As pH falls below 2, a layer of silica gel residue (SiO_2) is the only compound left behind on the surface of the deteriorated concrete sample. Degradation of concrete subjected to acid attack is represented qualitatively in Fig. 4 (Grube and Rechenberg 1989).
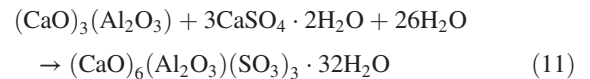
Limited information is available on the effects of organic acids on concrete, but the general mechanisms are the same as for any acid attack. The decrease in surface tension shown by organic compounds tends to increase the diffusion of the acidic solutions into the concrete pores, causing deterioration (Zivica 2006). Some fungi and bacteria present on the sewer walls can excrete organic acids which degrade the concrete (Gu et al. 1998).
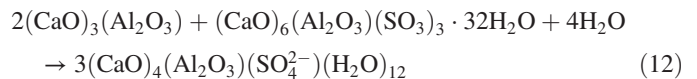
Sulfuric Acid Attack

Sulfuric acid attack can be classified as a combined sulfate and acid attack. Transformation of calcium hydroxide to calcium sulfate (gypsum) and ettringite formation are typical of sulfate attacks:

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 \cdot 2H_2O \tag{10}$$

Calcium hydroxide + Sulfuric acid → Gypsum

$$(CaO)_3(Al_2O_3) + 3CaSO_4 \cdot 2H_2O + 26H_2O$$
$$\rightarrow (CaO)_6(Al_2O_3)(SO_3)_3 \cdot 32H_2O \tag{11}$$

Tricalcium aluminate + hydrated gypsum + water → Ettringite

$$2(CaO)_3(Al_2O_3) + (CaO)_6(Al_2O_3)(SO_3)_3 \cdot 32H_2O + 4H_2O$$
$$\rightarrow 3(CaO)_4(Al_2O_3)(SO_4^{2-})(H_2O)_{12} \tag{12}$$

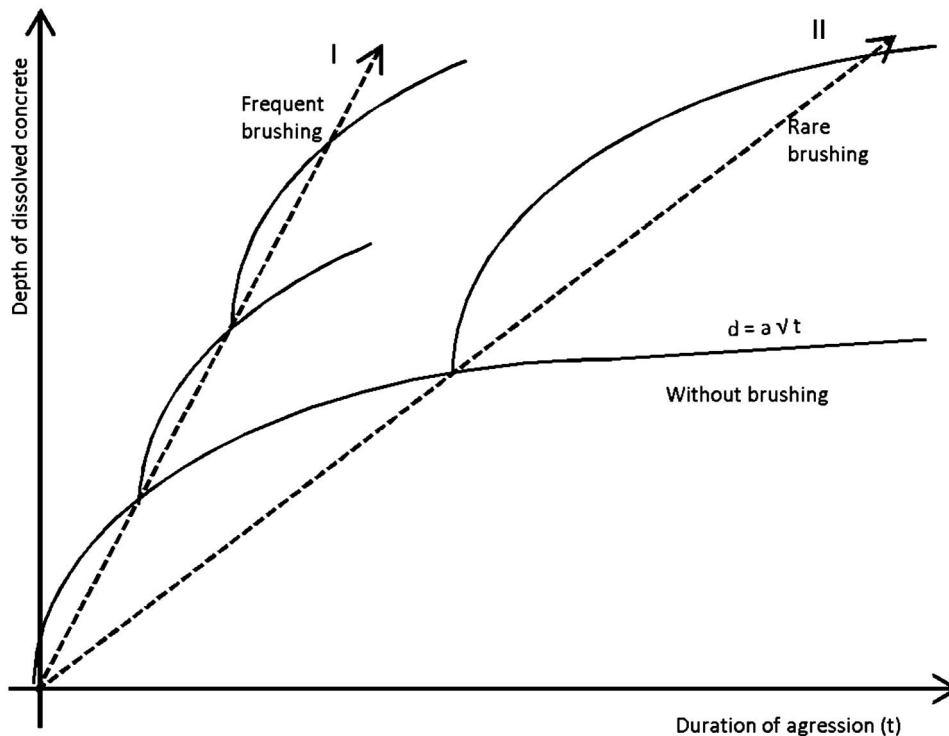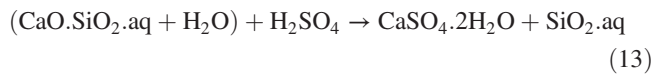Tricalcium aluminate + ettringite + water → Monosulfoaluminates

Fig. 4. Deterioration depth of concrete subjected to acid attack (reprinted from Grube and Rechenberg 1989, with permission from Elsevier)

Conversion of C-S-H into hydrous silica ($SiO_2.aq$) is a sign of acid attack:

$$(CaO.SiO_2.aq + H_2O) + H_2SO_4 \rightarrow CaSO_4.2H_2O + SiO_2.aq \tag{13}$$

Calcium silicate hydrate + sulfuric acid → Gypsum + hydrous silica residue

A low w/c ratio is generally the main parameter for predicting durability, but with the data found in the literature, it is difficult to predict the effect of sulfuric acid attack on a given concrete mixture based on its w/c ratio, density, or permeability. The concentration of the acid may be a better classification for the attack. Attacks with 2% sulfuric acid solution showed no differences between degradation of high and low porosity mortar paste sample (Israel et al. 1997); 1% sulfuric acid solution showed greater degradation for low w/c ratios than high w/c ratios samples (Fattuhi and Hughes 1988). Finally, low sulfuric acid concentrations (0.0016 and 0.02%) showed greater deterioration depth for samples with low w/c ratios than with high w/c ratios (Hughes and Guest 1978).

Deterioration Rates

Biodeterioration rates are calculated as the thickness of material lost over time. In biodeterioration rates based on laboratory experiments, the initial pH reducing phase of concrete biodeterioration is not always taken into account. Little information on the duration of this initiation period is available in the literature.

Biodeterioration rates for different in situ and laboratory conditions for specimens are compared in Table 1. Steady-state biode-

terioration rates may be helpful for an initial estimate of concrete sewer pipe life expectancy, but do not account for changes in wastewater flow, temperature, and composition.

Lumped Deterioration Models

Steady-state biodeterioration of concrete can be predicted using the following relationship representing the rate of attack of biogenic sulfuric acid on concrete (EPA 1992):

$$r_{empirical} = 0.45\phi_{sw}\, k/A \tag{14}$$

where $r_{empirical}$ = empirical baseline biodeterioration rate (in./year); ϕ_{sw} = H_2S flux to the concrete (g of S/m^2h), A = alkalinity of the material as $CaCO_3$ equivalent ($gCaCO_3/g$ concrete, dimensionless); and k = an empirical constant between 0.3 and 1.0 that is related to the efficiency of the reaction. A conversion factor for the units is 0.45 and it is an empirical coefficient. The alkalinity of the material is a measure of the calcium carbonate content of the cement and the aggregates (De Belie et al. 2004). According to this equation, a sample with a greater alkalinity will have a smaller biodeterioration rate when all other parameters are constant since more material is available for neutralization.

Peak biodeterioration rates (r_{peak}, in in./year) can be estimated by multiplying the average biodeterioration rate ($r_{empirical}$) with appropriate factors. The crown biodeterioration factor (CBF) accounts for the location of biodeterioration and the turbulence biodeterioration factor (TBF) accounts for turbulence caused by junctions and drops:

Table 1. Biodeterioration Rate of Concrete Sewer Pipe and Mortar Specimen

Characteristics				Biodeterioration rate		Reference
Type of samples	Location of experiment	Duration	H$_2$S concentration			
			ppm	mm/year	Location	
Concrete sewer pipe	Treatment plant	14 years	5-400	4.3–4.7	Water line	Mori et al. (1992)
				1.4	Crown	
				0	Bottom	
Mortar samples w/c ratio: 0.65	Treatment plant (in manhole)	8 months	5–400	5.7	—	
	Demonstration plant	10 months	25–300	7.6	—	
	Laboratory	6 months	≈400	6.1	Sewage level	
				3.8	Submerged samples in medium for bacterial growth	
				0	Submerged samples in water	
Concrete sewer pipes	For modeling purposes, from literature review			3		Roberts et al. (2002)
Concrete sewer pipe Concrete samples w/c ratio: 0.34 to 0.41	In-situ, samples taken from sewer pipe in service	12 years		1.1–1.8		Vincke et al. (2002)
	Laboratory	2 months (4 cycles of 17 days)	250 for 3 days of each cycle	1.6–4.3	Concrete samples with cyclic exposure conditions to mimic worst case in situ conditions (Table 9-2)	
		3.6 months (9 cycles of 12 days)	0	Up to 2.7	Chemical test with removal of deterioration products by brushing	
Concrete samples	Laboratory	~1 month (3 cycles of 12 days)	250 for 3 days of each cycle	Up to 5.7	Concrete samples with cyclic exposure conditions to mimic worst case in situ conditions (Table 9-2)	Vincke et al. (1999)
Mortar samples w/c ratio: 0.40	In-situ	1 year	30 ± 20	3–4	Inside manhole	Okabe et al. (2007)

$$r_{\text{peak}} = r_{\text{empirical}} * \text{CBF} * \text{TBF} \qquad (15)$$

By equating the average biodeterioration rate to the amount of concrete which can be lost over the expected service life of a pipe (generally taken as the concrete cover), the combined life factor, $A \cdot z$, is defined. If L = service life of the pipe (in years), and z is the concrete cover (in inches):

$$z/L = 0.45\phi_{sw}\, k/A \qquad (16a)$$

and, by rearranging

$$A \cdot z = 0.45\phi_{sw}\, kL \qquad (16b)$$

This factor allows for a more efficient use of material from pipe manufacturer, since the concrete cover can be adjusted based on the alkalinity in the available materials (Kineow 1977).

De Belie et al. (2004) found that the correlation between biodeterioration measured in laboratory settings and the calculated biodeterioration rates could be improved by adding another input variable, water absorption of samples, as:

$$r_{\text{empirical}} = c_1/A + c_2 W \qquad (17)$$

where c_1 and c_2 = model coefficients and W = water absorption (% by mass of the concrete specimen), and all other variables are as defined for Eq. (13). Here, c_1 is an amalgamated coefficient representing the $(0.45\phi_{sw}\, k)$ term in Eq. (13). The inclusion of the water absorption of samples would take into account the effects of casting and curing of the concrete because these are the main parameters influencing its water absorption capacity.

Process or Mechanistic Deterioration Models

Process or mechanistic modeling uses a system of differential equations to predict the growth of bacteria (Grady et al. 1999); it also considers the various physical and chemical phenomena that occur in the modeled system. Presently, the design of water treatment plants uses process modeling.

General Concepts

To grow, microorganisms need a source of carbon, a source of energy (electron donor) and a final electron acceptor. The microorganisms using organic molecules as a source of carbon are heterotrophs, while those using carbon dioxide or other inorganic compounds are autotrophs. The microorganisms derive their energy, used for maintenance, growth or production of new bacteria, from the oxido-reduction reaction (transfer of an electron from a donor to an acceptor). When the final electron acceptor is oxygen, microorganisms are aerobic; other final electron acceptors can be nitrite or sulfide. When microorganisms can thrive only in environments devoid of oxygen, they are anoxic (when nitrite or nitrate are used as electron acceptors) or anaerobic (when electron acceptors other than oxygen, nitrite and nitrate are used). Some may use oxygen when it is present or other compounds when it is not, they are then facultative. Sulfate respiration is anaerobic and uses organic carbon as the carbon source and electron donor.

Dissolved oxygen (DO) in the wastewater controls the aerobic or anoxic/anaerobic condition of the wastewater and underwater biofilms. This DO is transferred from the atmosphere to the wastewater by aeration according to Henry's law and mass-transfer limitation. The reaeration rate of wastewater is a function of the overall mass-transfer coefficient, which is dependent on the physical and hydraulic conditions of the sewer (Froude number, pipe slope, and flow velocity). The driving force for the reaeration rate is the difference between the saturated and actual dissolved oxygen concentrations of the wastewater. The higher is this difference, the faster will be the reaeration rate.

Biofilms will form on the surface of the concrete under the wastewater and above in the sewer atmosphere. When biofilms are deep, top layers are aerobic because of the oxygen transfer, while bottom sections are anaerobic. Underwater biofilms can be completely anaerobic if not enough dissolved oxygen is present in the wastewater to aerate the top layers of the biofilm. Oxygen travels to deeper regions of the biofilm by diffusion.

Process Modeling of Gravity Sewers

Heterotrophic growth of bacteria in wastewater and underwater biofilms, both aerobic and anaerobic, is well understood and is the basis for the wastewater aerobic-anaerobic transformation in sewers (WATS), which includes formation of sulfides in wastewater (Hvitved-Jacobsen 2002). Additional modules for emission of hydrogen sulfide to the sewer atmosphere and its subsequent oxidation on the sewer walls are summarized in the following, and also in a conceptual model in Fig. 5.

Sulfide Production by Sewer Biofilms

Sulfates are converted to sulfides by the microorganisms in the wastewater, or in the biofilms growing on the sewer walls. Typically, wastewater will have sulfate concentrations between 20 and 50 mg/L. Domestic water use may increase the concentration of sulfates in the wastewater stream by 15 to 30 mg/L (Metcalf and Eddy 2003).

Microbial sulfide production is anaerobic; usually, it does not occur in the wastewater and takes place only in the deep, nonoxygenated regions of the biofilms growing on the submerged wall of the pipe. Transport of organic compounds (electron donors), or the presence of dissolved oxygen can be limiting. Hvitved-Jacobsen (2002) modeled the sulfide production rate in underwater biofilms assuming nonlimiting sulfate concentrations. The sulfides produced diffuse outward to the bulk wastewater.

Chemical and Biological Sulfide Oxidation

Sulfides can be oxidized in the underwater sewer biofilms and in the bulk wastewater under aerobic conditions; however, oxidation of sulfide to sulfate may or may not occur in a system depending on the dissolved oxygen concentration in the wastewater.

Sulfide oxidation in underwater biofilms was investigated by Nielsen et al. (2005). Oxidation was modeled by a power equation dependent on the dissolved oxygen and sulfide concentrations.

In the wastewater, oxidation and dependency on temperature and pH were investigated by Nielsen et al. (2006). The optimal pH range for oxidation was very close to the in situ pH values of wastewater (around 8). Oxidation was also modeled as being dependent on dissolved oxygen and sulfide concentrations, with oxidation products ranging from elemental sulfur to sulfates and thiosulfates. However, the reaction rates were highly variable from one wastewater sample to another and appropriate numerical values could not be recommended. This may be because biological oxidation reactions are dependent on the active biomass concentration. This was not considered in the model and active biomass concentrations can be expected to vary widely from one sample to another. In summary, it is important to realize that a model estimation of the active biomass concentration at one location can only be estimated by simulating the entire sewer system. Consequently, the overall design features of a sewer network may influence local concrete degradation rates.
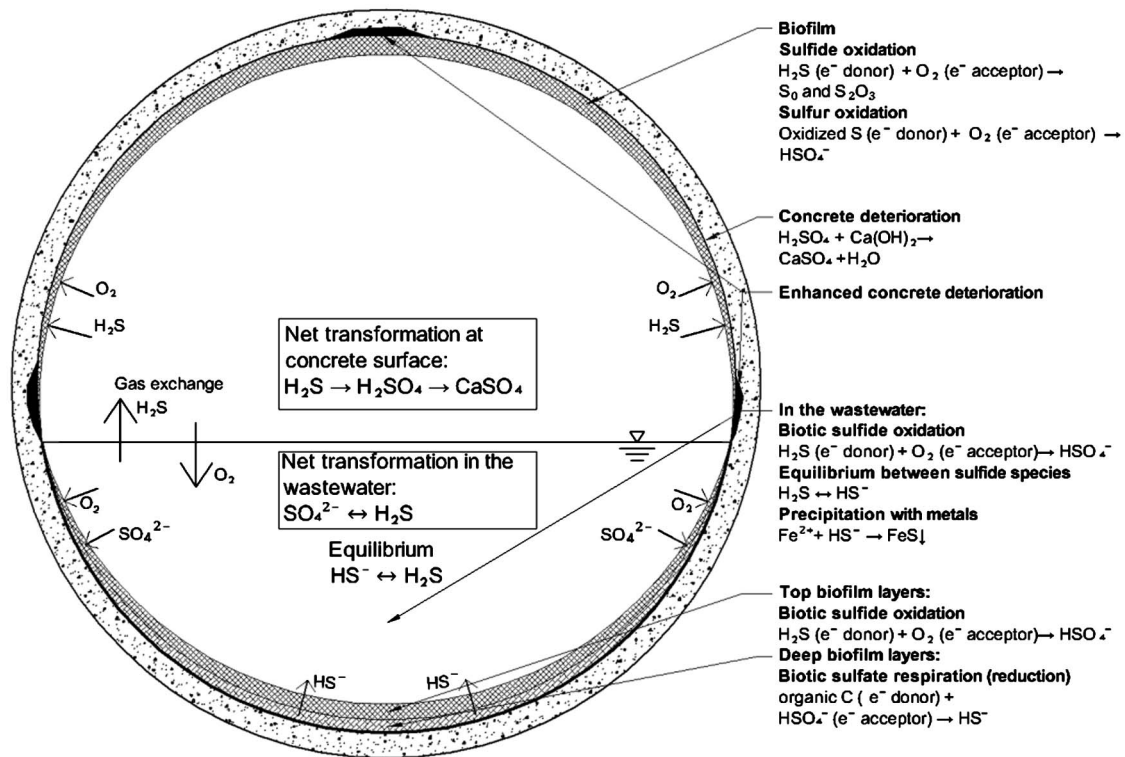
Fig. 5. Conceptual model of processes involved in biodeterioration in a sewer pipe as a bioreactor (not to scale); biofilm thickness has been exaggerated to show processes

Precipitation of Sulfide with Metals

Metals react with sulfides in the sewer and precipitate, reducing the amount of sulfide available for oxidation or emission to the atmosphere. The implementation of industrial source control programs and EPA National Industrial Categorical Pretreatment of 1977 in the United States caused a reduction of heavy metals in sewers, and is generally acknowledged to have increased the biodeterioration of concrete sewer pipes (Padival et al. 1995); the WATS model does not take into account the precipitation of sulfides with metals.

Iron, zinc, lead, and copper are the ions most commonly responsible for precipitation with sulfides in the wastewater (Yongsiri et al. 2003). Iron will precipitate most readily with sulfides, based on its higher solubility constant (Lange et al. 2005).

Sulfide Emission from Water Phase to Headspace of Sewer

The rate of sulfide emission to the sewer atmosphere is proportional to the difference between the amount of sulfides present as hydrogen sulfide, and the maximum possible concentration of H_2S in the atmosphere (saturation concentration, according to Henry's law). Only undissociated hydrogen sulfide can be emitted from the water phase. Equilibrium between H_2S, HS^-, and S^{2-} is dictated by the acid dissociation constant (K_a) of hydrogen sulfide (pK_a, $-\log K_a$, of 7 and 19 for first and second dissociation) (Zumdahl 1998). Fig. 6 shows the percentage of each species based on pH values. At typical pH values for wastewaters, both H_2S and HS^- species will be present.
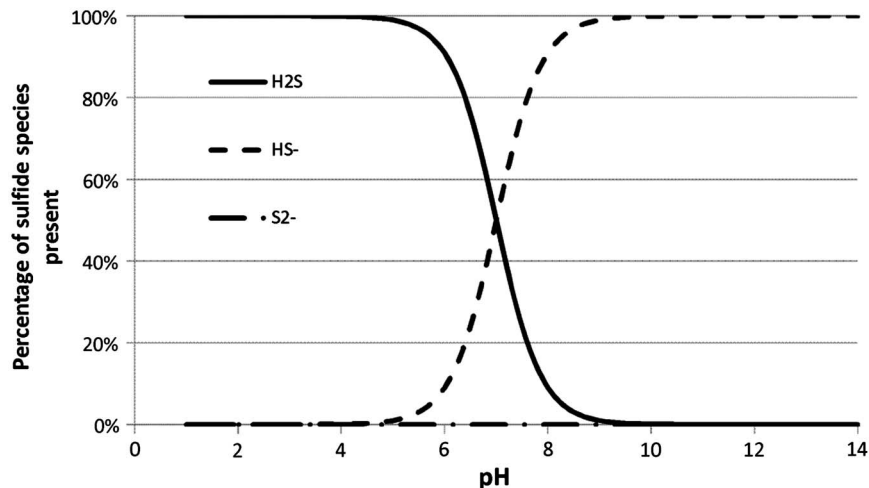

Fig. 6. Species of sulfur present based on pH

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Hydrogen Sulfide Oxidation on Sewer Walls

In the unsubmerged biofilms exposed to the atmosphere, the environment is aerobic. Hydrogen sulfide is available as the electron donor; carbon source can be organic molecules (from splashing of the sewage on the sewer walls), or carbon dioxide (from the atmosphere). The microbial succession in the unsubmerged biofilms, during the active biodeterioration stage, is summarized in Table 2. For this environment, two general categories of microorganisms can be differentiated based on their preferred growth media:
- Neutrophilic sulfur-oxidizing microorganisms (NSOM), which thrive at pH near neutral and are found at the onset of biodeterioration; and

- Acidophilic sulfur-oxidizing microorganisms (ASOM), which prefer acidic media.

Three different deterioration states are normally noted as: not visibly deteriorated, slightly deteriorated, and heavily deteriorated. The formation of the deterioration layer, composed mainly of gypsum in the heavily deteriorated state, may allow greater microbial colonization because of its porosity (higher surface area to volume ratio) and its ability to retain moisture (Monteny et al. 2000). Some microorganisms can produce organic acids (other than biogenic sulfuric acid), that can also attack the concrete.

The oxidation of sulfur compounds can be chemical or biological. Fig. 7 summarizes the two possible oxidation processes in the sewer air space, which can occur concurrently (Islander et al. 1991). The nomenclature of sulfur compounds shown in

Table 2. Microorganisms Found in Unsubmerged Concrete Sewer Pipe Biofilms

Deterioration	Species	Growth pH Minimum/optimal/maximum	Electron donor utilized	Carbon source/ aerobic or anaerobic	Method of detection	Reference
Not visibly deteriorated	*Thiobacillus thioparus* (bacteria)	Min: 5–3.5/Opt: 6.6–7.2/Max: 9–10	HS^-, S^0, $S_2O_3^{2-}$, $S_4O_6^{2-}$ and $S_3O_6^{2-}$	Carbon dioxide, strictly aerobic	Culture-based	Islander et al. 1991
	Thiotrix sp. (bacteria)	N/A			16S rRNA-targeted gene sequencing FISH[a]	Okabe et al. 2007
Slightly deteriorated	*Fusarium* (fungus)	N/A			Culture-based	Gu et al. 1998
	Halothiobacillus neapolitanus (Bacteria) [formerly *Thiobacillus neapolitanus* (bacteria)]	Min: 2.8/Opt: 6.5–6.9/Max: 8.5	HS^-, S^0, $S_2O_3^{2-}$, $S_4O_6^{2-}$ and $S_3O_6^{2-}$	Carbon dioxide, strictly aerobic	Culture-based	Islander et al. 1991
	Starkeya novella (bacteria) [formerly *Thiobacillus novellus*]	Min: 5.7/Opt: 7.0/ Max: 9.0	S^0, $S_2O_3^{2-}$, $S_4O_6^{2-}$	Organic substrate, strictly aerobic	Culture-based	Islander et al. 1991
	Thiomonas intermedia (bacteria) (formerly *Thiobacillus intermedius*)	Min: 2.0–2.8/Opt: 5.5–6.0/Max: 7.5	HS^-, S^0, $S_2O_3^{2-}$, $S_4O_6^{2-}$	Organic substrate, aerobic	16S rRNA-targeted gene sequencing FISH culture-based	Okabe et al. 2007, Islander et al. 1991, Gu et al. 1998
	Thiobacillus plumbophilus (bacteria)	Min: 4.0/Opt: N/A/ Max: 6.5	HS^-	Carbon dioxide, strictly aerobic	16S rRNA-targeted gene sequencing FISH	Okabe et al. 2007
Heavily deteriorated	*Acidithiobacillus thiooxydans* (Bacteria) (formerly *Thiobacillus thiooxydans*)	Min: 0.5/Opt: 2.0–3.0/Max: 5.5	S^0 (rapidly), $S_2O_3^{2-}$ (to SO_4^{2-})	Carbon dioxide, strictly aerobic	16S rRNA-targeted gene sequencing FISH culture-based	Islander et al. 1991, Okabe et al. 2007, Cho and Mori 1995, Nica et al. 2000, Hernandes et al. 2002
	OMSOf1 (fungus)	Min: 0.5/Opt: neutral/Max: N/A	HS^- (to $S_2O_3^{2-}$)	N/AN/A	Morphological characteristics	Cho and Mori 1995
	Acidiphilium acidophilum (bacteria) (formerly *Thiobacillus acidophilus*)	Min: 1.5/Opt: 3.0–3.5/Max:6.0	S^0, $S_2O_3^{2-}$, $S_4O_6^{2-}$ and $S_3O_6^{2-}$	Organic matter, strictly aerobic	16S rRNA-targeted gene sequencing FISH	Okabe et al. 2007
	Acidithiobacillus ferrooxidans (bacteria) (formerly *Leptospirillum ferrooxydans* and *Thiobacillus ferrooxidans*)	Min: 1.3/Opt: 2.5/ Max: 4.5	S^0, $S_2O_3^{2-}$ and $S_4O_6^{2-}$	Carbon dioxide, strictly aerobic	16S rRNA-targeted gene sequencing Polymerase Chain Reaction FISH	Hernandes et al. 2002 Okabe et al. 2007

Note: Italics from Bergey's *Manual of Systematic Bacteriology* (Bergey et al. 2005).
[a]FISH: Fluorescent in situ hybridization.

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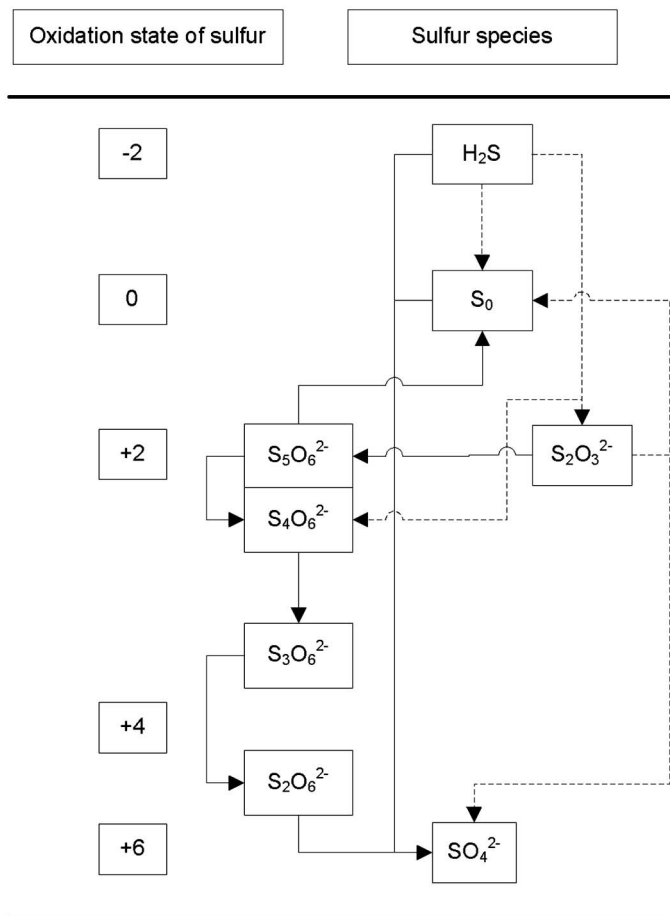J. Pipeline Syst. Eng. Pract., 2011, 2(2): 42-52

Fig. 7. Sulfur oxidation states typical in sewer; biologic pathway is shown with full lines; chemical, with dashed lines. (Islander et al. 1991, ASCE)

Fig. 7 is found in the appendix. Most sulfur-oxidizing microorganisms are not able to oxidize sulfides directly; elemental sulfur deposits are often found on the surface of concrete subjected to biodeterioration. A good correlation was noted between the observed data and modeling of the initial chemical transformation of hydrogen sulfide to elemental sulfur, and then biotic oxidation to sulfuric acid (Jensen et al. 2009).

Deterioration of Concrete

The reactions between concrete and sulfuric acid occur at this stage. As explained earlier, concrete deterioration caused by sulfuric acid attack will depend on the concentration of the acid, cement content (availability of alkaline-rich material to be neutralized) and the concrete permeability (ingress of aggressive elements into concrete).

Æsøy et al. (2002) used a Monod type equation to model concrete biodeterioration rates as a function of the hydrogen sulfide gas concentration in the sewer atmosphere (Fig. 8). This relationship was based only on three data points, including null biodeterioration at null hydrogen sulfide concentration. Prediction of concrete biodeterioration with values of $H_2S_{(gas)}$ concentration does not consider the additional sulfide transformations described earlier.

Future Research Needs

The basic processes involved in biodeterioration of concrete are still not fully understood, mostly because microorganisms produce other kinds of biogenic acids which may not have exactly the same
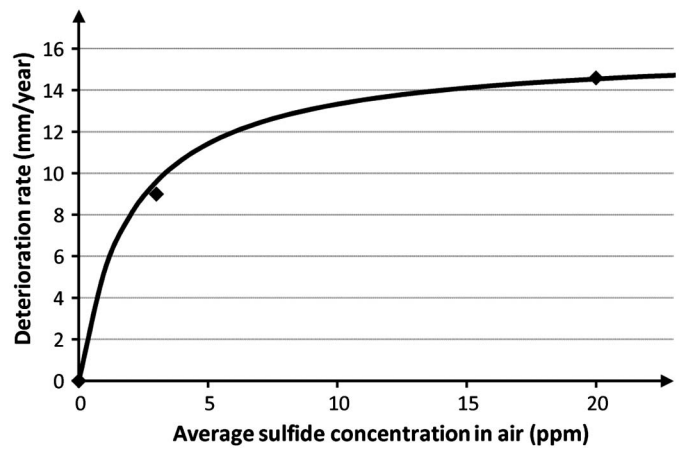

Fig. 8. Predicted and measured biodeterioration rate based on concentration of hydrogen sulfide present in the sewer atmosphere (reprinted from Æsøy et al. 2002, with permission from IWA Publishing)

effect on concrete as sulfuric acid. Sulfuric acid concentration may be a better estimate of the strength of the attack than any other concrete parameters.

Models for biodeterioration of concrete sewer pipes are still relatively crude. Further research is needed to validate the use of the improvement presented by De Belie et al. (2004). The rates of acid production and penetration into the concrete have not been modeled chemically, although some research has been performed with generic acid attacks (Beddoe and Dorner 2005). A moving-boundary system, modeling corrosion in sewer pipes, was developed by Böhm et al. (1998). However, several of the assumptions are not fully borne out, and the numerical values of some parameters lack an adequate degree of reliability.

Further research on microorganisms is needed: the exact microbial ecology supporting long-term acid production is unknown (Hernandez et al. 2002); similarly, the knowledge of the growth rates of the different microorganisms involved is relatively scarce (Nica et al. 2000). Researchers have hinted that gypsum, since it is very porous and is able to provide moisture, may enhance the deterioration process (Monteny et al. 2000).

A research program is under way at McGill University to gather more information on biodeterioration of concrete sewer pipes based on a conceptual understanding of the various processes occurring in sewers. The WATS model presented by Hvitved-Jacobsen (2002) will be used as a starting point, and the reactions between concrete and deleterious substances will be added. Neutralization of the hydrated cement paste in the initiation stage needs to be included in the conceptual model as a preliminary phase. Additional steps in the sulfur cycle, such as precipitation of sulfides with metals and concrete deterioration, must be included in the WATS model. The use of a Monod type equation for concrete deterioration does not rely on much data. Its validity needs to be confirmed, before it is included in the model.

Appendix: Sulfide Oxidation States and Nomenclature

Symbol	Oxidation state of sulfur ion	Name
H_2S	−2	Hydrogen sulfide
HS^-	−2	Dissociated hydrogen sulfide
S^{2-}	−2	Sulfide

Symbol	Oxidation state of sulfur ion	Name
S^0	0	Elemental sulfur
$S_2O_3^{2-}$	+2	Thiosulfate
$S_5O_6^{2-}$	+2	Pentathionate
$S_4O_6^{2-}$	+2.5	Tetrathionate
$S_3O_6^{2-}$	+3.33	Trithionate
$S_2O_6^{2-}$	+5	Dithionate
SO_4^{2-}	+6	Sulfate
HSO_4^-	+6	Dissociated sulfuric acid
H_2SO_4	+6	Sulfuric acid

Notation

The following symbols are used in this paper:

A = alkalinity of the material as $CaCO_3$ equivalent (g of $CaCO_3$/g of concrete, dimensionless);

CBF = crown biodeterioration factor ranging from 1.5 to 2.0;

c_1 and c_2 = model coefficients in Eq. (15);

k = empirical constant related to the efficiency of the reaction between sulfuric acid and concrete with a value between 0.3 and 1.0;

L = pipe service life (years);

$r_{empirical}$ = empirical baseline biodeterioration rate (in./year);

r_{peak} = peak empirical baseline biodeterioration rate (in./year);

TBF = turbulence biodeterioration factor, ranging from 1.0 to 2.5 for well-designed junctions and 5.0 to 10.0 for drops, or turbulent junctions;

W = water absorption (% by mass of the concrete specimen);

z = concrete cover (in.); and

ϕ_{sw} = H_2S flux to the concrete (g of S/m^2 h).

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