A review of sulfide emissions in sewer networks: overall approach and systemic modelling
Lucie Carrera, Fanny Springer, Gislain Lipeme-Kouyi and Pierre Buffiere

ABSTRACT
The problems related to hydrogen sulfide in terms of deterioration of sewer networks, toxicity and odor nuisance have become very clear to the network stakeholders and the public. The hydraulic and (bio)chemical phenomena and parameters controlling sulfide formation, emission and their incidences in sewer networks are very complex. Recent research studies have been developed in gravity and pressure sewers and some transfer models have been published. Nevertheless, the models do not take into account all the physical phenomena influencing the emission process. After summing up the main scientific knowledge concerning the production, oxidation, transfer and emission processes, the present review includes: (i) a synthetic analysis of sulfide and hydrogen sulfide emission models in sewer networks, (ii) an estimation of their limit, (iii) perspectives to improve the modelling approach. It shows that sulfide formation and uptake models still need refinements especially for some phenomena such as liquid to gas mass transfer. Transfer models that have been published so far are purposely simplified and valid for simple systems. More efforts have to be undertaken in order to better understand the mechanisms and the dynamics of hydrogen sulfide production and emission in real conditions.

Key words | H₂S oxidation, H₂S production, liquid-gas transfer, sewer system modelling

SYMBOLS

<table>
<thead>
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<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>a</td>
<td>ratio of water surface area to water volume (m⁻¹)</td>
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<tr>
<td>a’</td>
<td>ratio to biofilm area to bulk water volume (m⁻¹)</td>
</tr>
<tr>
<td>b</td>
<td>pipe width (m)</td>
</tr>
<tr>
<td>Cₐ,L</td>
<td>concentration of species A in liquid phase (mol.L⁻¹)</td>
</tr>
<tr>
<td>Cₐ,G</td>
<td>concentration of species A in gas phase (mol.L⁻¹)</td>
</tr>
<tr>
<td>Cₐ,L,i</td>
<td>concentration of species A in liquid phase at interface (mol.L⁻¹)</td>
</tr>
<tr>
<td>Cₐ,G,i</td>
<td>concentration of species A in gas phase at interface (mol.L⁻¹)</td>
</tr>
<tr>
<td>Cₐ,G,s</td>
<td>concentration of species A in liquid phase at saturation (mol.L⁻¹)</td>
</tr>
<tr>
<td>Cₛ</td>
<td>total sulfide concentration (gS.m⁻³)</td>
</tr>
<tr>
<td>dₘ</td>
<td>hydraulic mean depth, defined as the water cross-section area divided by the width of the water surface (m⁻¹)</td>
</tr>
<tr>
<td>Dₘ</td>
<td>molecular diffusion coefficient of species A</td>
</tr>
<tr>
<td>f</td>
<td>ratio of H₂S to total sulfide (-)</td>
</tr>
<tr>
<td>Fₛₚ</td>
<td>sulfide surface flux (gS.m⁻².h⁻¹)</td>
</tr>
<tr>
<td>Fₛₜ</td>
<td>flux of hydrogen sulfide (g.m⁻².h⁻¹)</td>
</tr>
<tr>
<td>F</td>
<td>Froude number, F = u/(g.dₘ)⁰.⁵</td>
</tr>
<tr>
<td>g</td>
<td>gravitational constant (9.81 m.s⁻²)</td>
</tr>
<tr>
<td>G</td>
<td>velocity gradient (s⁻¹)</td>
</tr>
<tr>
<td>H</td>
<td>Henry’s law constant (atm.mol.fraction⁻¹) or Pa.L.mol⁻¹ or Pa.m³.mol⁻¹</td>
</tr>
<tr>
<td>H’</td>
<td>Henry’s law constant (-)</td>
</tr>
<tr>
<td>k</td>
<td>Strickler constant (-)</td>
</tr>
<tr>
<td>Kₘ</td>
<td>water reaeration coefficient (m⁻¹)</td>
</tr>
<tr>
<td>Kₗ</td>
<td>overall liquid transfer rate coefficient (m.h⁻¹)</td>
</tr>
<tr>
<td>kₗ</td>
<td>mass transfer coefficient in the liquid layer (m.h⁻¹)</td>
</tr>
<tr>
<td>kₘ</td>
<td>mass transfer coefficient in the gas layer (m.h⁻¹)</td>
</tr>
<tr>
<td>kox,c</td>
<td>rate constant for chemical sulfide oxidation (m³.gO₂⁻¹.d⁻¹)</td>
</tr>
<tr>
<td>kox,b</td>
<td>rate constant for biological sulfide oxidation (gS⁻⁰.⁵.m.(gO₂)⁻⁰.⁵.d⁻¹)</td>
</tr>
<tr>
<td>L</td>
<td>pipe length (m)</td>
</tr>
<tr>
<td>M’</td>
<td>coefficient (gS.gO₂⁻¹.m.h⁻¹)</td>
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<table>
<thead>
<tr>
<th>Symbol</th>
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<tr>
<td>N coef</td>
<td>coefficient (-)</td>
</tr>
<tr>
<td>n exp</td>
<td>exponent (-)</td>
</tr>
<tr>
<td>N_A</td>
<td>mass flux (g.h⁻¹.m⁻²)</td>
</tr>
<tr>
<td>N_A'</td>
<td>volumetric mass flux (g.h⁻¹.m⁻³)</td>
</tr>
<tr>
<td>P'</td>
<td>wetted wall pipe perimeter (m)</td>
</tr>
<tr>
<td>P_{H2S}</td>
<td>H₂S partial pressure in the sewer gas phase (atm)</td>
</tr>
<tr>
<td>Q</td>
<td>flow rate (m³.h⁻¹)</td>
</tr>
<tr>
<td>R</td>
<td>hydraulic radius i.e. the cross-sectional area of the water volume divided by the wetted perimeter (m)</td>
</tr>
<tr>
<td>R_{ox,c}</td>
<td>chemical sulfide oxidation (gS.m⁻².d⁻¹)</td>
</tr>
<tr>
<td>R_{ox,b}</td>
<td>surface specific sulfide oxidation rate (gS.m⁻².d⁻¹)</td>
</tr>
<tr>
<td>R_{st}</td>
<td>rate of sulfide elimination (mg.L⁻¹.s⁻¹)</td>
</tr>
<tr>
<td>s</td>
<td>slope (m.m⁻¹)</td>
</tr>
<tr>
<td>S_L</td>
<td>liquid surface (m²)</td>
</tr>
<tr>
<td>t</td>
<td>time (t)</td>
</tr>
<tr>
<td>t_R</td>
<td>the retention time corresponding to the mixing period (s)</td>
</tr>
<tr>
<td>T</td>
<td>wastewater temperature (K or °C)</td>
</tr>
<tr>
<td>u</td>
<td>mean flow velocity (m.s⁻¹)</td>
</tr>
<tr>
<td>V_L</td>
<td>liquid volume (m³)</td>
</tr>
<tr>
<td>W</td>
<td>dissipation function (N.s⁻¹.m⁻²)</td>
</tr>
<tr>
<td>x</td>
<td>length (m)</td>
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**Greek symbols**

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<thead>
<tr>
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<th>Definition</th>
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<tbody>
<tr>
<td>α</td>
<td>ratio of K_L in polluted water to that in clean water (-)</td>
</tr>
<tr>
<td>β</td>
<td>ratio of solubility in polluted water to that in clean water (-)</td>
</tr>
<tr>
<td>λ</td>
<td>constant in Colebrook-White equation (-)</td>
</tr>
<tr>
<td>ΔHx</td>
<td>the head loss in a straight pipe of length x (m)</td>
</tr>
<tr>
<td>ε₁, ε₂</td>
<td>constant (-)</td>
</tr>
<tr>
<td>θ₁, θ₂</td>
<td>temperature correction constants (-)</td>
</tr>
<tr>
<td>γ</td>
<td>unit weight of liquid (for fresh water, 104 N.m⁻³)</td>
</tr>
<tr>
<td>μ</td>
<td>dynamic viscosity (for water = 10⁻³ N.s.m⁻² at 20 °C)</td>
</tr>
<tr>
<td>ν</td>
<td>kinematic viscosity (for pure water = 10⁻⁶ m².s⁻¹ at 20 °C)</td>
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**List of Abbreviations**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>BOD</td>
<td>biochemical oxygen demand (gO₂.m⁻³)</td>
</tr>
<tr>
<td>COD</td>
<td>chemical oxygen demand (gO₂.m⁻³)</td>
</tr>
<tr>
<td>COD₇</td>
<td>filtered COD (mg.L⁻¹)</td>
</tr>
<tr>
<td>DO</td>
<td>dissolved oxygen (mg.L⁻¹)</td>
</tr>
<tr>
<td>SRB</td>
<td>sulfate-reducing bacteria</td>
</tr>
<tr>
<td>cw</td>
<td>clean water</td>
</tr>
<tr>
<td>ww</td>
<td>wastewater</td>
</tr>
</tbody>
</table>

**INTRODUCTION**

A sewer network is an integral part of the urban wastewater system including the pipes, the wastewater treatment plant and the receiving water bodies. Since progressive transformation of organic and inorganic matter occurs, it is essential to understand the phenomena occurring in these systems to support the water resource quality and the sustainability of urban engineering structures. This implies understanding the physical, chemical and biological processes in sewer networks. Anaerobic microbial processes are known to be responsible for the formation of undesirable, often odorous substances, such as volatile organic compounds and hydrogen sulfide (H₂S), which is the target molecule of the present study. The sulfur cycle is complex because of the variety of oxidation states of sulfur and the difficulty of predicting the chemical and biological phenomena (Figure 1).

Sulfide is produced in anaerobic zones (pressure mains or stagnant zones) by sulfate-reducing bacteria (SRB). Under anaerobic conditions encountered in gravity sewers, H₂S can be emitted into the atmosphere or precipitated in the liquid phase. The major problems related to sulfide buildup in sewers include: (i) corrosion of sewer structures, (ii) odor nuisance and (iii) health impacts on sewer workers (US EPA 1974; Nielsen et al. 1992). Understanding the fate of sulfide is thus a major issue for a better management of sewer systems.

The relation between concrete corrosion and hydrogen sulfide emission was identified more than a century ago. Concrete corrosion is costly for the communities because it requires an accelerated rehabilitation and pipe replacement frequency (Sydney et al. 1996).

Hydrogen sulfide is likely to be emitted from the water phase and to contaminate the atmosphere in manholes, gravity sewers and wet-wells of pumping stations. This gas is recognizable by its rotten egg odor and can engender complaints by the local residents, notably in urban areas. In addition, several human health-related problems are potentially associated with the occurrence of H₂S. A simplified estimation of seriousness for sulfide concentration is ‘minor’ below 0.5 mgS.L⁻¹, and ‘medium’ and ‘considerable’
for respective concentrations in wastewater ranging between 0.5 and 3 mgS.L\(^{-1}\) and higher than 3 mgS.L\(^{-1}\). However, even minor hazard situations should be taken care of properly (Hvitved-Jacobsen 2002).

Knowledge-based models are needed to improve the design and the management of wastewater collection systems. They are expected to predict sulfide concentrations and should be used as decision support tools for control practices. Existing models include the description of each major process (production, equilibrium in solution, transfer, oxidation, etc.), but still remain limited in terms of applicability. The main problems are: (i) the difficulty of quantifying the processes under real conditions; (ii) the temporal and spatial variability of the phenomena; (iii) the limited possible conditions of experimental observations; and (iv) the numerical modelling. Major transformation and transport phenomena in sewer systems have been reviewed in the literature (Hvitved-Jacobsen et al. 2002). Our objective here was to focus on a critical analysis of the existing models for sulfide production and emission in order to identify the key research orientations for a better management of sewer networks.

**SULFIDE FORMATION**

**Sulfide formation process**

A sewer network is a complex system, variable in time and space (Sharma et al. 2013). Biological sewer processes are dominated by heterotrophic microorganisms that transform wastewater components under favorable conditions (pH, biodegradability of the organic matter and active biomass) (Nielsen et al. 1992). These processes occur in the liquid phase, the biofilms and the sediments (Bjerre et al. 1998; Hvitved-Jacobsen et al. 1998). The mechanism for sulfide production is sulfate respiration by heterotrophic bacteria (Figure 1). Sulfate-reducing species are able to metabolize a wide range of organic compounds using sulfate as final electron acceptor (Nielsen & Hvitved-Jacobsen 1988). According to Zhang et al. (2008), sulfate concentration in domestic wastewaters typically ranges between 40 and 200 mg.L\(^{-1}\), (13.2 to 66 mg.L\(^{-1}\) of S). The global reaction can be summarized as follows:

\[
SO_4^{2-} + \text{organic carbon} \Rightarrow CO_2 + H_2S
\]  

Sulfate reduction only occurs in anaerobic conditions, in full-flowing gravity sewers, pressure mains and stagnant zones. It primarily takes place in the biofilm and the sediments.

**Parameters impacting the sulfide formation**

Anaerobic conditions and nitrate (or other oxidized inorganic compounds) are needed for sulfide formation. Sulfides are usually not present in the bulk water at dissolved oxygen (DO) concentrations >1 mg.L\(^{-1}\). Oxygen depletion is usually associated with low redox potential in the wastewater: optimal conditions for sulfate reduction range from \(-500\) to \(-200\) mV (reported to the standard hydrogen electrode).
At dissolved sulfate concentrations higher than 5–15 gS.m$^{-3}$ (15–50 mg.L$^{-1}$ sulfate) and a thin biofilm, the sulfide formation is not limited (Nielsen & Hvitved-Jacobsen 1988).

Biodegradable organic matter is the electron donor for SRB. In domestic wastewaters, readily biodegradable chemical oxygen demand (COD) may be abundant, which generates a high potential for sulfide formation (Nielsen & Hvitved-Jacobsen 1988).

Temperature is a key parameter since sulfate reduction is a biological process. Sulfide formation rates can be hampered in wastewaters at temperatures between 5 and 12 °C (in this situation much higher residence times in anaerobic conditions are required for a significant sulfide buildup) and stimulated above 15 °C. Substrate diffusion in the biofilms also depends on the temperature (Nielsen et al. 1998). Finally, optimal pH for the growth of the SRB mainly lies between 5.5 and 9 (Gutierrez et al. 2009).

Hydrodynamic conditions influence biological activity of the SRB via the biofilm thickness and the anaerobic residence time. At low velocity ($u < 0.8$ m.s$^{-1}$), thick biofilms may grow (100–300 µm) and a greater deposition of sediment occurs (Santry 1965). At higher velocities, the biofilm is thinner due to the shear forces, and the resistance to mass transfer is reduced. In addition, low velocities result in longer residence times, increasing the likelihood of anaerobic conditions. The anaerobic residence time should typically exceed 0.5–2 hours before sulfide build up is significant (Hvitved-Jacobsen 2002). Flow variations also cause diurnal fluctuations in the formation of sulfide. Moreover, the area to volume ratio in sewer pipes can affect the sulfide concentration.

Modelling sulfide formation

Considerable attention has been paid to the modelling of sulfide formation in the last decades since it provided strong support to water utilities for a cost-effective sulfide management (Thistlethwayte 1972; Boon & Lister 1975; Hvitved-Jacobsen et al. 1988). The flux of sulfide produced, $F_{sp}$, is given in gS.m$^{-2}$.h$^{-1}$ (Table 1), linked to the biofilm surface and the liquid volume.

The equation for the expression of the produced sulfide is (Hvitved Jacobsen 2002):

$$C_{S_2, \text{ inlet}} - C_{S_2, \text{ outlet}} = F_{sp} \times a \times t_R$$

Models for the prediction of sulfide formation include the concentration of organic matter (biochemical oxygen demand (BOD) or COD) in the wastewater as a key parameter. They are established for raw water with high organic matter

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Empirical equations for sulfide production in pressure mains</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flux at 20°C ($F_{sp}$ at 20°C) (gS.m$^{-2}$.h$^{-1}$)</td>
<td>References</td>
</tr>
<tr>
<td>----------------------------------------------------------</td>
<td>---------------------------------------------------------------</td>
</tr>
<tr>
<td>$0.5 \times 10^{-3} u \cdot BOD^{0.8} \cdot \varepsilon \cdot S_0 \times 1.059^{T-20}$</td>
<td>(3) Thistlethwayte (1972)</td>
</tr>
<tr>
<td>$0.228 \times 10^{-3} COD \times 1.07^{T-20}$</td>
<td>(4) Boon &amp; Lister (1975)</td>
</tr>
<tr>
<td>$M' \cdot BOD \times 1.07^{T-20}$</td>
<td>(5) Pomeroy &amp; Parkhurst (1977)</td>
</tr>
<tr>
<td>$M' = 1.10^{-3}$ gS.gO$_2$.m.h$^{-1}$ (Hvitved-Jacobsen 2002)</td>
<td>(6) Hvitved-Jacobsen et al. (1988)</td>
</tr>
<tr>
<td>$M' = 0.32 \times 10^{-3}$ gS.gO$_2$.m.h$^{-1}$ (original Pomeroy equation, 1977)</td>
<td></td>
</tr>
<tr>
<td>$\epsilon_1 = 0.0015$ typical Danish domestic wastewater without industrial sewage</td>
<td></td>
</tr>
<tr>
<td>$\epsilon_1 = 0.003$ wastewater from mixed domestic and industrial (foodstuff) sources</td>
<td></td>
</tr>
<tr>
<td>$\epsilon_2 = 0.006$ wastewater mainly from foodstuff industries</td>
<td></td>
</tr>
<tr>
<td>$\epsilon_2 = 0.001-0.002$ typical Danish domestic wastewater without industrial sewage</td>
<td></td>
</tr>
<tr>
<td>$\epsilon_2 = 0.0005-0.0006$ wastewater from mixed domestic and industrial (foodstuff) sources</td>
<td></td>
</tr>
<tr>
<td>$\epsilon_2 = 0.0007-0.001$ wastewater with biodegradable organic matter from mainly foodstuff industries</td>
<td></td>
</tr>
<tr>
<td>$1.52 \times 10^{-2} COD \times \left(1 + 0.004D\right)$</td>
<td>(7) Nielsen et al. (1998)</td>
</tr>
<tr>
<td>$0.0025 \times 10^{-3} COD \times 1.07^{T-20}$</td>
<td>(8) Boon (1995)</td>
</tr>
<tr>
<td></td>
<td>(9) Elmaleh et al. (1998)</td>
</tr>
</tbody>
</table>
content (500–1,000 mg.L⁻¹ of total COD) and high sulfate concentration (above 4–5 mgS.SO₄²⁻.L⁻¹) (Equations (4)–(7)). Equation (9) was obtained with field data with mean total COD of 72 mg.L⁻¹, DO 3.3 mg.L⁻¹, and Reynolds number 240,000 (Kitagawa et al. 1998). Equations (6) and (7) account for the origin of the wastewater.

Even in the presence of oxygen, local anaerobic areas in the biofilm may produce sulfide due to mass transfer limitation. Norsker et al. (1995) established sulfide production rates from 15 to 70 mgS.m⁻².h⁻¹ (with the highest rate found in biofilms grown at DO below 1 mg.L⁻¹: 80 mgS.m⁻².h⁻¹ at 20 °C). Those rates correspond to the conversion of approximately 170 mg COD.m⁻².h⁻¹, assuming a yield coefficient for SRB of 0.05 (Okabe et al. 1992; Nielsen et al. 1998). Other authors found lower sulfide production rates in a 12 m long and 2.1 cm diameter gravity pipe (0.5 mgS.m⁻².h⁻¹, Nielsen et al. 2005a).

Pomeroy & Parkhurst (1977) proposed Equation (10) for the prediction of sulfide formation:

\[
F_{sp} = M'BOD \times 1.07^{(T-20)} - N(su)^{3/8} \times d_m^{-1} \times \rho \times RC_{S^2-L}
\]  

(10)

The possible oxidation of H₂S in the water phase and its release into the sewer atmosphere may also be included in the models (Pomeroy & Parkhurst 1977; Wilmot et al. 1989). Equation (10) is composed of a first term similar to Equation (5), corresponding to the sulfide formation rate, and a second term expressing the loss of sulfide in the water phase caused by oxidation and uptake. Sulfide formation rate was found to be lower in a gravity sewer than in a pressure main, so the \( M' \) value is usually lower than given by Equation (5). The \( N \) coefficient is an adjustable parameter varying from 0.64 to 0.96. Matos & de Sousa (1992) used Equation (11) to predict sulfide concentration providing that the downstream conditions are known.

\[
C_{S^2-inlet} = \frac{M'BOD(su)^{3/8}(P')}{N} - \left( C_{S^2-outlet} \times \frac{M'}{N} \times BOD(su)^{3/8}(P') \right) 
\times \exp \left( -\frac{LNs^{5/8}}{3600d_mu^{0.625}} \right)
\]  

(11)

Most empirical models were developed in the 1970s for the prediction of the H₂S generation in sewers. They were primarily established at laboratory scale and show limitations in terms of applicability, mainly because they lump several factors influencing H₂S production into a single rate expression, and neglect many processes of in-sewer (bio)transformations: diffusion in the water phase, chemical or biological oxidation, and metal sulfide precipitation (Zhang et al. 2008).

### Sulfide Oxidation and Precipitation

Since H₂S is a weak acid (pKₐ₁ = 7 and pKₐ₂ = 13 at 25 °C), sulfide may be present in aqueous solutions in the form of S²⁻, HS⁻ and H₂S. S²⁻ is generally neglected except at very high pH values, and H₂S is predominant below 7 (Churchill & Elmer 1999).

The ratio \( f \) between dissolved H₂S and total sulfide concentrations can be calculated from Equation (12) (Lahav et al. 2006):

\[
f = \frac{C_{H₂S}}{C_S} = \frac{1}{1 + 10^{pH - pK_a1} + 10^{pH - pK_a1 - pK_a2}}
\]  

(12)

Sulfide oxidation to elemental sulfur or sulfate involves chemical and biological processes. Schematically, the main equations are:

\[
2O₂ + H₂S \rightarrow SO₄²⁻ + 2H^+
\]  

(13)

\[
HS^- + 2O₂ \rightarrow SO₄²^- + H^+
\]  

(14)

\[
2HS^- + O₂ \rightarrow 2S^- + 2OH^-
\]  

(15)

Equation (13) describes a microbial transformation occurring at pH below 5 (Hvitved Jacobsen 2002) while the transformations described by Equations (14) and (15) may be due to either chemical or biological processes. This point is not well described in the literature. Predominantly, sulfide is oxidized to thiosulfate, though this reaction is very slow (Jørgensen 1990). A part of sulfide is also oxidized to elemental sulfur (Lefers et al. 1978; Okabe et al. 1998). This oxidation is possible at acidic or neutral pH (Jensen et al. 2012; Joseph et al. 2012). The process kinetics of chemical and biological sulfide oxidation in wastewater can be described according to Equation (16) (Nielsen et al. 2005a; Sharma et al. 2008), and the chemical oxidation of sulfide with oxygen under controlled conditions
can be described by a first order model (Equation (17)) (O’Brien & Birkner 1977):  
\[
R_{ax,c} = k_{ax,c} C_{S^{2-}} \cdot L C_{O_{2,L}} 
\]  
(16)  
\[
R_{ax,c} = 4.46 \times \frac{C_{O_{2,L}}}{1.5 + C_{O_{2,L}}} \times C_{H_2S,L}^{0.56} 
\]  
(17)  
Sulfide biological oxidation can be expressed by the model proposed by Nielsen et al. (2005a):  
\[
R_{ax,b} = k_{ax,b} \sqrt{C_{S,L} \cdot C_{O_{2,L}} \cdot a'} 
\]  
(18)  
In the liquid phase and in the biofilm, sulfide may precipitate as insoluble metal sulfides (Hvitved-Jacobsen 2002; Nielsen et al. 2005b). Therefore, iron salts can be added to wastewater either under ferric or ferrous forms to control \( \text{H}_2\text{S} \) emissions through precipitation (Jameel 1989). Zhang et al. (2008) clearly presented new approaches for hydrogen sulfide emission control in sewer systems. The main solutions come down to: (i) increase the redox potential to control the sulfide formation, (ii) inhibit the SRB activity, (iii) chemically remove sulfide by precipitation or oxidation.

**MODELLING THE SULFUR CYCLE IN SEWERS**

Bjerre et al. (1998) first proposed a model for microbial carbon transformations in sewer systems. The model included biomass growth, hydrolysis and decay of particulate biomass. Biofilm and sediment processes were included as simple surface flux equations. The development of the WATS model (Wastewater Aerobic/Aerobic Transformation in Sewers) (Nielsen et al. 1992, 1998, 2006; Tanaka & Hvitved-Jacobsen 1998; Hvitved-Jacobsen et al. 2000, 2002; Tanaka et al. 2000a) relies on a conceptual description of the sulfur cycle in gravity sewers and pressure mains and links the sulfur cycle to a dynamic modelling of the carbon cycle in terms of mass transport, transformation and interfacial exchange in the water, the biofilm and the gas phase. Other modelling approaches, such as structured model based on (bio)chemical mass balance, have been developed in order to represent the evolution of the transformations occurring in sewers (Sharma et al. 2008).

In the WATS model, each process is represented by a steady state equation and stoichiometric coefficients describing:

- the transformation of organic matter (Hvitved-Jacobsen 2002);
- the emission of \( \text{H}_2\text{S} \) in the sewer atmosphere and the subsequent oxidation on moist walls (Jensen 1995);
- the kinetics of chemical and biological sulfide oxidation (Wilmot et al. 1989; Tanaka et al. 2000b).

Three fractions of sulfide are considered:

- the dissolved sulfide (\( \text{H}_2\text{S} + \text{HS}^- \));
- the particulate sulfide including various metal sulfides;
- the gaseous hydrogen sulfide, calculated from the partial pressure of hydrogen sulfide in the sewer atmosphere.

The description of the model for aerobic and anaerobic transformations was summarized by Hvitved-Jacobsen (2002). Additional details concerning the sulfur cycle processes were described by Nielsen et al. (2005a, 2005b). The WATS model was successfully calibrated and validated to simulate the carbon cycle in sewers against field measurements (Almeida et al. 1999). Model simulations of sulfide buildup in forced mains were also proven feasible (Nielsen et al. 1998). Nielsen et al. (2006) reported a field study where the model was able to predict the sulfide concentrations in forced mains and gravity sewers. Tanaka et al. (2000a, 2000b) have obtained sulfide production rates in biofilms ranging from 0.067 to 0.166 gS.m\(^{-2}\).h\(^{-1}\)(20 °C), similar to Norsker et al. (1995) (0.08 gS.m\(^{-2}\).h\(^{-1}\) at 20 °C).

Some limits can be stressed: (i) this model is mostly applicable to steady flows, (ii) flow and air turbulence influence is not systematically included, (iii) the sulfide production in suspended biofilms is neglected, (iv) each process is described by an equation independently chosen by the authors among a large panel of empirical equations. Due to considerable variations of the wastewater quality, the water flow and the anaerobic residence time, it is essential to include temporal and spatial variations into the models, as proposed by Sharma et al. (2008). Rising mains were modelled as a series of reactors to mimic a plug flow in a real sewer pipe. Under dry weather, intermittent flow due to pumping operations was recreated.

Concerning the sulfide production, the double Monod kinetics presented by Freudenthal et al. (2005) was used with volatile fatty acids and sulfate as substrates (Sharma et al. 2008). The maximal interfacial sulfide production rate was obtained and calibrated at 10 gS.m\(^{-2}\).day\(^{-1}\).

**HYDROGEN SULFIDE TRANSFER**

The mass transfer of \( \text{H}_2\text{S} \) from the liquid phase is the key process of \( \text{H}_2\text{S} \) emission. The overall description of the \( \text{H}_2\text{S} \) emission still remains partial. A large number of
laboratory-scale investigations were achieved (US EPA 2001; Lahav et al. 2004; Yongsiri et al. 2004a, 2005), added to field applications (Lahav et al. 2004). Some of them were based on oxygen transfer measurements (assuming a relationship between the H₂S and the O₂ transfer). Others investigated the relation between mass transfer and hydrodynamic parameters. Published work in this field may have two objectives: (i) the determination of the H₂S emission rate and (ii) the determination of the overall mass transfer coefficient.

Background

According to the two-film theory (Lewis & Whitman 1924), the interfacial mass flux \( N_A \) can be written as the product of the mass transfer coefficient, either in the liquid layer \( (k_L) \) or in the gas layer \( (k_G) \), and the concentration gradient:

\[
N_A = k_L(C_{A,L} - C_{A,L,I}) = k_G(C_{A,G,I} - C_{A,G})
\]  

Similarly to oxygen, the mechanism of H₂S transfer is assumed to be controlled by the mass transfer in the liquid film since both gases exhibit a low solubility in water and a high Henry constant. Since the interfacial concentrations cannot be easily measured, the following relation is frequently used:

\[
N_A = K_L(C_{A,L} - C_{A,L,I})
\]  

The driving force is the difference between the concentration in the liquid phase \( C_{A,L} \) and the saturation \( C^S_{A,L} \) which depends on the Henry’s law constant. The mass flux can also be expressed relative to the liquid volume by taking into account the interfacial area \( a \) (the interfacial area divided by the corresponding liquid volume) and Equation (20) reduces to:

\[
N'_A = k_LA(C_{A,L} - C_{A,L,I}/H)
\]  

From Equation (21), several parameters may affect the liquid–gas mass transfer:

- the specific interfacial area \( (a = S_L/V_L) \) conditioned by the flow turbulence (through interface deformation), and by the geometry and the structure of the hydraulic system.

To conclude, the mass transfer is controlled by physical parameters: temperature, hydraulics, aeraulics (Yongsiri et al. 2005); and chemical parameters: pH, dissociation equilibrium of H₂S, water and sewer gaseous content (Blunden et al. 2008).

Parameters influencing hydrogen sulfide transfer

Temperature

Temperature is positively correlated to the molecular diffusivity, the Henry’s law constant, the acid constant, and the viscosity. The overall mass transfer increases with temperature. The Henry’s law constant only depends on temperature in clear water (Roustan 2003). Consequently, the ratio between the species concentration in the liquid phase and in the gas phase decreases. The most frequent value implemented for clear water is 513.1 ± 15.1 atm.mol fraction⁻¹ and for wastewater is 525 ± 16.4 atm.mol fraction⁻¹ (Yongsiri et al. 2005). Matos & de Sousa (1992) proposed an empirical model linking the concentration of hydrogen sulfide gas at equilibrium to the concentration of sulfide in liquid bulk in closed vessels containing dissolved hydrogen sulfide, under normal atmospheric conditions:

\[
C_{H_2S,G} = \left(3.79 \times 10^{-2} T^2 + 7.64 \times 10^{-3} T + 0.197\right) C_{H_2S,L}
\]  

The expression of the overall mass transfer coefficient introduces a correction factor \( \Theta \) to standardize the temperature values at 20 °C (Jensen & Hvitved-Jacobsen 1991):

\[
K_{L,H_2S}(20°C)a = K_{L,H_2S}(T) \Theta^{(T - 20)}.
\]  

Wastewater composition

Since wastewater composition influences the O₂ mass transfer, it is reasonable to suppose that it also influences the H₂S liquid–gas transfer (Yongsiri et al. 2005). Yongsiri et al. (2004a) coupled the temperature effect to the sulfide dissociation by establishing a correction factor \( \Theta_c \):

\[
\Theta^{(T - 20)} = \frac{1 + 10^{pH - pKa_s(20°C)}}{1 + 10^{pH - pKa_s(T)}} \Theta^{(T - 20)}.
\]
The influence of pH on sulfide liquid–gas transfer is well understood and modelled (Equation (12)).

Yongsiri et al. (2004a) determined the $\Theta_c$ parameter as 1.0340 for pH 4.5, and 1.0286 and 1.0212 for pH 6.5 and 7 respectively. The value of 1.034 was also selected in other articles and generally assimilated to $\theta$ (Yongsiri et al. 2005).

Based on the standard O$_2$ transfer approach (US Environmental Protection Agency 1974), the effect of wastewater components on the transfer rate is represented by the $\alpha$ and the $\beta$ correction factors for the overall mass transfer coefficient and the saturation concentration, respectively:

$$\frac{dC_{H_2S,L}}{dt} = \alpha k_{La} (\beta C_{H_2S, L}^* - C_{H_2S,L}),$$

$$\alpha = \frac{K_{H_2S,L,w} a}{K_{H_2S,L,cw} \Theta_c}$$

and

$$\beta = \frac{C_{H_2S, w}}{C_{H_2S, cw}}$$

The H$_2$S transfer rate in wastewater is 32–46% lower than in deionized water (Yongsiri et al. 2004a; Yongsiri et al. 2005). The values obtained were $\alpha = 0.60–0.62$ (with standard deviations of 0.05–0.08) and $\beta = 0.95$ to 1.

The effect of conductivity was assessed to be insignificant for the H$_2$S transfer (US Environmental Protection Agency 1974, Yongsiri et al. 2004a). Furthermore, impurities in domestic wastewater were concluded not to have a significant impact on the Henry’s law constant and the O$_2$ transfer, in accordance with Al-Haddad et al. (1989) experiments. Also, surfactant substances near the liquid–gas interface can affect the surface tension and the liquid–gas transfer (O’Connor 1965).

Design and hydrodynamics

In sewer network systems, hydrogen sulfide transfer mainly occurs in waterfalls and in gravity pipes. The wastewater flow principally depends on the mass flow, the pipe slope, the pipe geometry and the frictional resistance (Hvitved-Jacobsen 2002). Each parameter may vary with space and time. The mass flow is directly linked to the pumping time and the pumping capacity. It fluctuates and may turn the flow regime into subcritical or supercritical. The pipe slope can change locally due to local topography. The frictional resistance varies according to concrete degradation.

In gravitational pipes, the turbulence intensity plays a role at the interface and is controlled by the pipe slope and the wall characteristics (Lahav et al. 2004, 2006) (see Appendix, available with the online version of this paper). A high slope (>1%) and high velocity conditions result in an important ratio of volume area exposed to the atmosphere and in a decrease in the boundary layer, enhancing the transfer process.

H$_2$S release in a waterfall is linked to the O$_2$ release:

$$\ln \left( \frac{C_{H_2S,L_{inlet}}}{C_{H_2S,L_{outlet}}} \right) = K_H \times L \frac{C_{H_2S,L}}{C_{O_2,L}}$$

with $C_{H_2S,L}$ estimated as 0.91 (Reid et al. 1977; Tanaka et al. 2000b).

The characteristics of the sewer atmosphere

The concentration of H$_2$S in the gas phase has an impact on the emission rate via the saturation concentration $C_{A,L}$ (Equation (20)), influenced by the movement of the air phase along the sewer (Yongsiri et al. 2004a). With insufficient ventilation, H$_2$S (density 1.18) will accumulate in the vicinity of the liquid–gas interface. For simplification purpose, the impact of the gas phase concentration on the transfer is often neglected. Argo et al. (1999) noted that the $k_{La}$ appeared independent of the wind velocity, while Schmidt & Bicudo (2002) considered that the H$_2$S concentration was dependent on the wind speed.

Using the WATER9 model for the calculation of the mass transfer coefficients, the volatilization of hydrogen sulfide was shown to be approximately constant at low speed, i.e. when friction velocity is lower than 0.5 m.s$^{-1}$, from investigations on quiescent liquid surfaces under laboratory conditions (Santos et al. 2012).

EXISTING MODELS FOR HYDROGEN SULFIDE TRANSFER

Two main approaches are developed in the literature: (i) empiric or theoretical connections between oxygen and hydrogen sulfide transfer coefficients, (ii) empiric models linking the sulfide emission to flow parameters.

Empirical equation linking O$_2$ and H$_2$S transfer coefficients

Since the DO level in sewer systems is a parameter governing most biophysicochemical phenomena in sewer
networks, \( \text{O}_2 \) is often taken as a model compound. Generally, the water-air transfer of gaseous substances is related to the emission of \( \text{O}_2 \). Indeed, this question has been addressed in many research works for the characterization of the aeration efficiency in wastewater treatment systems (activated sludge). The connection between the mass transfer coefficients ratio \( \frac{K_L a_{\text{H}_2\text{S}}}{K_L a_{\text{O}_2}} \) and the liquid phase diffusion coefficients ratio \( \frac{D_m \text{H}_2\text{S}}{D_m \text{O}_2} \) (Equation (29)) was often assumed and confirmed (Liss & Slater 1974; Hvitved-Jacobsen 2002), with the purpose of using the oxygen transfer measurements in gravity sewers to estimate the \( \text{H}_2\text{S} \) transfer rate in the same conditions.

\[
\frac{K_L a_{\text{H}_2\text{S}}}{K_L a_{\text{O}_2}} = \left( \frac{D_m \text{H}_2\text{S}}{D_m \text{O}_2} \right)^n .
\]  

In this expression, \( n \) is not well defined from a theoretical point of view. Experimentally, \( n \) is about 1 in a sewer with a laminar flow and close to 0.5 under turbulent flow conditions. The diffusion coefficient ratio is assumed to be between 0.72 and 0.84 with a mean value of 0.84 (Hvitved-Jacobsen 2002; Yongsiri et al. 2005). This ratio was proved independent of the degree of mixing and equal to the theoretical value obtained from the literature.

The mass transfer coefficient is easier to measure for oxygen than for \( \text{H}_2\text{S} \). First, it can be assessed from the follow-up of DO concentrations and/or off-gases techniques and is commonly used for the characterization of the aeration efficiency in activated sludge (Capela et al. 2004). In addition, performing measurements with oxygen trigger fewer safety problems than with \( \text{H}_2\text{S} \). Finally, on-line measurement techniques for dissolved \( \text{H}_2\text{S} \) are not so commonly used. The six most relevant empirical models are gathered in Table 2.

Taghizadeh-Nasser (1986) worked at the laboratory scale. The other correlations were obtained from in situ measurements. Equations (30) and (31) were established in hydraulic conditions far from those typically encountered in gravity sewer systems. Parkhurst & Pomeroy (1972) (Equation (32)) and Jensen (1995) (Equation (33)) estimated \( K_{a,o} \) from investigations carried out in gravity sewers. Their model was frequently applied by US EPA (1985) and others to deal with hydrogen sulfide problems. The most frequently used model is the one proposed by Parkhurst & Pomeroy (1972), mentioned as the most relevant (Jensen 1995). However, in some applications of the WATS model, Equation (34) is used (Hvitved-Jacobsen et al. 2000; Tanaka et al. 2000b).

### Empirical equations and models linking \( \text{H}_2\text{S} \) transfer coefficient to parameters describing the flow

The Parkhurst & Pomeroy (1972) empirical equation (Equation (10)) was widely used for the prediction of the rate of sulfide in gravity sewers (Tanaka et al. 2000b). This equation is made of two terms: the first one predicts the sulfide buildup and the second one stands for the sulfide elimination from the liquid phase (including the biological oxidation and sulfide transfer in the sewer atmosphere):

\[
R_{st} = 0.64 (su)^{3\beta/8} C_{S,dm}^{-1} \]  

(rate of sulfide elimination in mg L\(^{-1}\) h\(^{-1}\)).

Assessing only the mass transfer, the flux of \( \text{H}_2\text{S} \) (\( F_{st} \)) is equal to the stream surface in sewer systems can also be described by Equation (36) (which is similar to Equation (10)) with an estimation of the \( K_{a,o} \):

\[
F_{st} = 0.69 (1 + 0.17F^{2}) (su)^{3\beta/8} C_{H_2S,L} \left( 1 - \frac{C_{H_2S,local}}{C_{H_2S}} \right) \]  

This equation accounts for the turbulence intensity and more specifically the effect of turbulence in comparison with a slow stream (Matos & de Sousa 1992).

Yongsiri et al. (2004a, 2005) reported an important work on the parameters influencing sulfide hydrogen mass transfer, involving a complete set of laboratory experiments. They edited the following equation (still based on the global mass transfer Equation (10)):

\[
\frac{dC_{H_2S,L}}{dt} = \alpha (0.86f) \left[ 0.86 + \left( 1 + 0.2F^2 \right)(su)^{3\beta/8} \right] \frac{C_{H_2S,L}}{d_{in}} \times \left[ C_{H_2S,L} - \beta \frac{C_{H_2S,S}}{H_{H_2S}} \right] \]  

This equation included the effects of temperature, wastewater quality (\( \beta \)), sewer characteristics and hydraulics (\( s, u, ...
The value of $\theta$ was fixed to 1.034. Yongsiri et al. (2004b) applied this model to partly filled gravity sewers. A similar structure was proposed by Lahav et al. (2006) (Equation (13)).

\[
\frac{dC_s}{dt} = 8.10^{-7} \frac{p_{St}}{\mu} \times a \times 1.024^{(T-20)} \left( \frac{C_s}{1 + 10^{pH-pKa_1} + 10^{pH-pKa_2-pKa_3} - P_{H_2S/H}} \right) \quad (38)
\]

The equation was calibrated and checked in various hydraulic conditions.

The mass transfer coefficient for the liquid phase $k_{fl}$ could first be calculated with the WATER 9 model. WATER9 takes physical and chemical parameters into account: the fetch-to-depth ratio, the wind speed, the hydrogen sulfide molecular diffusivity and the Schmidt number of the liquid flow. Santos et al. (2012) used this model to estimate the effect of the air flow velocity on the $H_2S$ liquid-gas transfer rate (Gostelow et al. 2001; US EPA 2001). The WATER9 model showed the best agreement with experimental data though it overestimated the overall mass transfer coefficient by a factor of up to 4.0.

The WATS model was applied by Tanaka et al. (2000b). It included the release of hydrogen sulfide in a waterfall (inspired by the expression of the oxygen transfer in a drop with a constant coefficient of 0.41 m$^{-1}$ according to US EPA (1985) and in a gravity pipe with the Parkhurst and Pomeroy equation (Equation (32))). In accordance with Yongsiri et al. (2003), the mass transfer process of hydrogen sulfide into the WATS model is represented via Equation (29) linking $K_{L,H_2S}$ to $K_{L,O_2}$, with $K_{L,O_2}$ modelled from Equation (34) (Jensen 1995).

\[
\text{REFERENCES}
\]


CONCLUSIONS AND PERSPECTIVES

- The description of sulfide formation and emission in sewer systems is still very difficult. In many cases, existing models lump together $H_2S$ buildup, oxidation, and emission as a single step.
- More recently, detailed models have separated the biochemical and/or chemical transformation from the emission processes. Nevertheless, there is still a lack of accuracy in the liquid to gas mass transfer description.
- More research is thus required in order to get a better description of mass transfer in hydraulic structures (gravity sewers, junctions or waterfalls).

- In addition, field measurements proved that concentration gradients could be significant both in the liquid and the gas phase. This result suggests a possible influence of air velocity. This parameter has not been investigated yet (Arogo et al. 1999; Lahav et al. 2004, 2006).


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