Modeling the corrosion of concrete sewers

J. Vollertsen¹*, A. H. Nielsen¹, H. S. Jensen², E. A. Rudelle¹, T. Hvitved-Jacobsen¹

¹) Department of Biotechnology, Chemistry and Environmental Engineering, Aalborg University, Sohngaardsholm's Vej 57, 9000 Aalborg, Denmark
²) Department of Chemical and Process Engineering, The University of Sheffield, Mappin Street S1 3JD, UK

* Corresponding author jv@bio.aau.dk

ABSTRACT
A conceptual model of concrete sewers corrosion is presented. The model is a two-phase flow model, simulating water and gas conveyance in sewers as well as transformation processes. The flow simulation is fully dynamic and process simulation takes carbon, sulfur and nitrogen into account. Release of hydrogen sulfide from the bulk water to the gas phase is modeled, as are kinetics of hydrogen sulfide transfer from the gas phase to the corroding concrete surface. The later takes gas flow turbulence into account. The corrosion itself is simulated by a novel conceptual approach, accounting for the sulfide and sulfur oxidizing biomass and for kinetics and stoichiometry of the involved processes. The model application is illustrated on an intercepting main consisting of a force main followed by a gravity main.

KEYWORDS
Hydrogen sulfide, modeling, concrete corrosion

INTRODUCTION
Some 100 years ago the first report on concrete sewers corrosion was published. Two decades later it was concluded that the cause of the corrosion was hydrogen sulfide (H₂S) from septic sewage. In the middle of the century, Parker (1951) formulated the first concrete corrosion concept and defined major process steps: Sulfide formation in the wet sewer compartment; H₂S release from the water to the gas phase; H₂S sorption by moist surfaces; Oxidation to sulfuric acid; Corrosion of concrete by the acid formed. Some decades later, Pomeroy and co-workers developed a model which corresponded to this understanding. Equation 1 (US EPA, 1974).

The US EPA (1974) corrosion model predicts the corrosion rate C in the unit of (mm year⁻¹). It assumes that the rate is proportional to the flux of H₂S to the pipe wall, F [g S m⁻² year⁻¹]. I.e. the more H₂S is absorbed by the concrete surface the greater the corrosion depth. However, not all absorbed H₂S ends up reacting with the alkaline concrete – accounted for by the concrete alkalinity, A [gCaCO₃ gConcrete⁻¹]. Only a fraction, k [-], of the H₂S absorbed reacts with the concrete. Finally, a material constant, a [m³ gCaCO₃ gConcrete⁻¹ gS⁻¹], is adopted accounting for process stoichiometry and concrete density.

The parameters a and A depend on the pipe material and are readily determined. However, the parameters F and k are more problematic. The flux of H₂S to the pipe wall, F, depends on a range of conditions, the first being the sulfide formation under anaerobic conditions, of which
part is precipitated by metal ions (Nielsen et al., 2005). Another part becomes biologically or chemically re-oxidized in the bulk water and biofilms by e.g. oxygen or nitrate (Nielsen et al., 2006). The later process depends mainly on constituent concentrations, catalysts and pH (Kotronarou and Hoffmann, 1991; Nielsen et al., 2008a). The H$_2$S that is not oxidized or precipitated is released to the sewer gas phase from where it is absorbed by moist surfaces or lost out of the system. The H$_2$S release rate depends on hydraulic conditions in the pipe, pH, wastewater constituents, and on H$_2$S gas phase concentrations (Pomeroy and Parkhurst, 1977). The transfer from the sewer gas to the moist surfaces depends on movement and turbulence in the gas phase as well as the surface conditions of the pipe (Hvitved-Jacobsen, 2002).

The parameter $k$ of the US EPA model accounts for the fraction of absorbed H$_2$S reacting with the concrete. H$_2$S is known to be oxidized to sulfuric acid via intermediates, especially elemental sulfur (Parker and Prisk, 1953; Jensen et al., in press). A significant part thereof is oxidized rather slowly and depending on system conditions, some might be lost into the bulk water. Furthermore, some of the formed sulfuric acid might drip back into the sewage with condense water or be washed off as a result of variations in the flow-depth (US EPA, 1974).

A number of studies have addressed sulfide formation, its fate in the bulk water and its release to the sewer gas phase. This work has been organized into model concepts, the first of which was the WATS concept originally presented in 1998 and continuously developed since (Hvitved-Jacobsen et al., 1998). Fewer studies have addressed the transfer of H$_2$S to the corroding concrete surface and the subsequent oxidation to sulfuric acid (Vollertsen et al., 2008a). The objective of this study is to present and apply the very first approach to a conceptual model of this part of the concrete corrosion process, describing the transport of H$_2$S from the sewer gas to moist sewer surfaces, and its oxidation to sulfuric acid via intermediates.

**METHODS**

The model is a further development of the WATS model concept (Vollertsen et al., 2008b) and consists of a hydraulic part rooting sewage and sewer gas through the network, of a phase-exchange part transporting compounds between the various phase-boundaries, and of a process part simulating the microbial and chemical transformations in the sewer phases. The numerical instant of the model is tailor-made for this application and programmed in Delphi Pascal™.

The force main simulation accounts for filling of the pump pit by a variable boundary flow and emptying of the pit by parallel operated pumps. In the force main, sewage plugs are followed at a time resolution of five seconds, as are the biological and chemical transformations. The discharge from the force main – in terms of flow and composition – is consequently simulated at the same resolution. The force main discharge is applied as upper boundary for the gravity main. Non-steady flow in the gravity main is simulated applying a full solution to the Saint-Venant equations and a double-sweep algorithm. Changes in wastewater composition are simulated by following plugs of sewage with a time resolution of one second.

**Gas movement**

The movement of the sewer gas phase in the gravity main is simulated as a fixed percentage of the water flow velocity. In sewer systems with closed manholes, the major driving force acting on the sewer gas is the drag of the flowing water. In such case, proportionality between water and gas velocity can be assumed as a first estimate of sewer gas movement (Bell et al., 1998;
Madsen et al., 2006). A more detailed solution to the gas movement can be obtained by applying a dynamic approach (Vorreiter and Wang, 2010; Hamer et al., 2010). However, at present only limited validation of such an approach has been published, and gas velocities are therefore calculated by the simplified assumption of a constant fraction of water velocities.

**Water phase processes**

Biological and chemical processes in sewer bulk water and biofilms are simulated as described by Vollertsen et al. (2008b). This approach includes the cycles of carbon, nitrogen, and sulfur in the sewer phases of bulk water, biofilms, and moist sewer surfaces. The model also simulates precipitation by metal salts and dosing of e.g. oxygen or nitrates. It has furthermore been extended by a flow-regime dependency of the \( \text{H}_2\text{S} \) formation. Little has been published on the dependency of the \( \text{H}_2\text{S} \) formation versus the flow regime, but for e.g. biofilm treatment plants it is known that transformation rates increase with increasing Reynolds number (Re) (Zhu and Chen, 2001). In the present model, the dependency of the \( \text{H}_2\text{S} \) formation rate (\( \text{r}_{\text{H}_2\text{S}} \)) on the flow regime is adapted from yet unpublished results, and described as a modified saturation type equation:

\[
\text{r}_{\text{H}_2\text{S}} = \text{r}_{\text{H}_2\text{S, max}} \cdot \left( \lambda + (1 - \lambda) \frac{\text{Re}}{\text{K}_{\text{Re}} + \text{Re}} \right),
\]

where \( \text{r}_{\text{H}_2\text{S, max}} \) is a maximum \( \text{H}_2\text{S} \) formation rate, \( \lambda \) is a number indicating the relative \( \text{H}_2\text{S} \) formation when the water stands still, and \( \text{K}_{\text{Re}} \) is a saturation type constant. The value of \( \lambda \) was chosen to 0.05 and \( \text{K}_{\text{Re}} \) to \( 10^4 \).

The oxygen transfer from sewer gas phase to water phase was simulated by the empirical oxygen transfer equation suggested by Jensen (1995). The \( \text{H}_2\text{S} \) emission from water to gas phase was simulated according to Yongsiri et al. (2004), taking \( \text{H}_2\text{S} \) dissociation into account.

**Sorption on concrete surfaces**

The \( \text{H}_2\text{S} \) transfer from sewer gas to concrete surface is a crucial step in the corrosion process. It governs how far \( \text{H}_2\text{S} \) is transported before being absorbed by a concrete surface. US EPA (1974) suggest setting the sorption of \( \text{H}_2\text{S} \) to the concrete surface equal to the bulk water \( \text{H}_2\text{S} \) release. I.e. all released \( \text{H}_2\text{S} \) is immediately absorbed by concrete surfaces, resulting in zero \( \text{H}_2\text{S} \) in the gas phase. However, transfer of \( \text{H}_2\text{S} \) from the gas phase to the concrete surface is not a momentary process and sorption kinetics should be taken into account. This is especially the case when predicting life times at e.g. force main discharge points or drop structures where release rates are higher than in other parts of the sewer. It is well-known that downstream of such locations the corrosion is more severe, and while knowledge on the water-gas transfer rate is a prerequisite for predicting extent and intensity of corrosion, it cannot stand alone.

The kinetics of \( \text{H}_2\text{S} \) sorption to corroding concrete has recently been reported by Vollertsen et al. (2008a) and Nielsen et al. (2008b) who presented results from a pilot rig constructed of Ø 200 mm concrete pipes. They showed that the sorption rate (\( F_{\text{H}_2\text{S}} \)) could be described as a power function in the gas phase \( \text{H}_2\text{S} \) concentration (\( P_{\text{H}_2\text{S}} \)) with powers \( n \) ranging between 0.5 and 0.8. Nielsen et al. (subm.a) showed that the sorption rate depends strongly on the gas flow regime. They presented an empirical relationship between the Reynolds number (Re) of the gas flow and the absorption rate: \( F_{\text{H}_2\text{S}} = k_a \text{Re}^{0.65} P_{\text{H}_2\text{S}}^n \)

**Oxidation of absorbed \( \text{H}_2\text{S} \) and subsequent corrosion**

Jensen et al. (2009) showed that in concrete corrosion products, \( \text{H}_2\text{S} \) is rapidly oxidized to a mix of elemental sulfur and sulfuric acid. If \( \text{H}_2\text{S} \) is continuously present, elemental sulfur accumulates and part converts into a slowly degradable form. I.e. they observed two
fractions of elemental sulfur, a readily degradable fraction which was oxidized at a rate similar to that of H$_2$S, and a slowly degradable fraction which was oxidized at a much slower rate. The slowly degradable elemental sulfur was seen to be degraded at a timescale of weeks to months, causing a delayed formation of sulfuric acid. These observations were confirmed by Nielsen et al. (subm.b) who operated six pilot rig reactors in parallel, each consisting of 2 m long Ø 200 mm concrete pipes. Each reactor was subdivided into 10 segments. The reactors were subjected to intermittent H$_2$S pulses – two reactors for 48 days, two reactors for 76 days and two reactors for 109 days. Here after the corrosion of every second segment was quantified. The rest of the segments were left untouched for 66 days after which the corrosion of the remaining segments was quantified. They observed that corrosion continued after H$_2$S exposure was terminated, and contributed this to slow oxidation of elemental sulfur present in the matrix formed by corrosion products. They could furthermore relate the corrosion efficiency factor $k$ of Equation 1 to the average H$_2$S surface loading, and found that this factor decreased with increasing surface load.

The work by Jensen et al. (2009) led to a model of the oxidation of sulfur compounds in a matrix of concrete corrosion products. Combining this with possible loss of sulfuric acid through condensed water and with possible loss of elemental sulfur by corrosion products detaching from the concrete surface, the concept shown in Figure 1 is derived.

![Figure 1. Conceptual model of the concrete corrosion process](image1)

![Figure 2. Calibration of the model to measured data reported by Nielsen et al. (subm.b)](image2)

The concept depicted in Figure 1 includes biological and chemical transformation pathways as well as growth kinetics and stoichiometry of the involved biomass. Jensen et al. (in press) further developed the concept and quantified biomass growth on H$_2$S. Combining the work of Jensen et al. (2009; in press) and Nielsen et al. (subm.b), the concept of corrosion presented below is suggested. Parameters are defined in Table 1.

\[
\frac{dS_{H_2S}}{dt} = -\frac{1}{Y_{H_2S}} r_1 + r_5 \\
\frac{dS_{s}^{0}}{dt} = \frac{1}{Y_{H_2S}} r_1 - \frac{1}{Y_{s}^{0}} r_2 - r_3 \\
\frac{dS_{s}^{0}}{dt} = r_3 + r_5 - \frac{1}{Y_{s}^{0}} r_6 \\
\frac{dS_{O_2}}{dt} = -\frac{0.5}{Y_{H_2S}} r_1 - \frac{1.5}{Y_{s}^{0}} r_2 - \frac{1.5}{Y_{s}^{0}} r_6 \\
\frac{dS_{H_2SO_4}}{dt} = \frac{1}{Y_{s}^{0}} r_2 + \frac{1}{Y_{s}^{0}} r_6 \\
\frac{dX_{SO_2}}{dt} = r_1 + r_2 + r_4 + r_6
\]
where

\[
    r_1 = \mu_{H_2S_{ox}} \frac{S_{H_2S}}{K_{H_2S_{ox}} + S_{H_2S}} \frac{S_{O_2}}{K_{O_2} + S_{O_2}} X_{SOB} \alpha^{T-20}
\]

\[
    r_2 = \mu_{SOB} \left( \alpha_{pres} \frac{S_{H_2S}}{K_{pres} + S_{H_2S}} + \frac{K_{abs}}{S_{H_2S}} \right) \frac{S_{S_f}^{ox}}{S_{S_f}} \frac{S_{S_f}}{X_{SOB}} + \frac{K_{abs} + S_{H_2S}}{K_{abs} + S_{H_2S}} X_{SOB} \alpha^{T-20}
\]

\[
    r_3 = z_S S_{S_f}^{ox}
\]

\[
    r_4 = b_{SOB} X_{SOB} \alpha^{T-20}
\]

\[
    r_5 = v_{abio} X_{TS}^{0.17} S_{H_2S_{ox}}^{1.17}
\]

\[
    r_6 = k_{S_f} \frac{S_{S_f}^{ox}}{K_{S_f} + \left( S_{S_f}^{ox} + S_{H_2S} \right)} \frac{S_{S_f}}{X_{SOB}} + \frac{K_{abs} + S_{H_2S}}{K_{abs} + S_{H_2S}} X_{SOB} \alpha^{T-20}
\]

### Table 1. Parameters used in the hydrogen sulfide oxidation model of corroding concrete

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Definition</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(S_{H2S})</td>
<td>Hydrogen sulfide</td>
<td>g H(_2)S-S</td>
<td>2</td>
</tr>
<tr>
<td>(S_{O2})</td>
<td>Dissolved oxygen</td>
<td>g O(_2) m(^{-3})</td>
<td>3</td>
</tr>
<tr>
<td>(S_{SOf})</td>
<td>Fast biodegradable elemental sulfur</td>
<td>g S m(^{-3})</td>
<td>4</td>
</tr>
<tr>
<td>(S_{SOs})</td>
<td>Slowly biodegradable elemental sulfur</td>
<td>g S m(^{-3})</td>
<td>5</td>
</tr>
<tr>
<td>(S_{H2SO4})</td>
<td>Sulfuric acid</td>
<td>g H(_2)SO(_4)-S m(^{-3})</td>
<td>6</td>
</tr>
<tr>
<td>(X_{SOB})</td>
<td>Sulfur oxidizing bacteria</td>
<td>g SOB m(^{-3})</td>
<td>7</td>
</tr>
<tr>
<td>(X_{TS})</td>
<td>Total solids</td>
<td>g TS m(^{-3})</td>
<td>8</td>
</tr>
<tr>
<td>(T)</td>
<td>Temperature</td>
<td>°C</td>
<td>9</td>
</tr>
<tr>
<td>(v_{abio})</td>
<td>Rate constant for abiotic H(_2)S oxidation(^a)</td>
<td>(g H(_2)S-S(^-3))(^{-1})</td>
<td>10</td>
</tr>
<tr>
<td>(\mu_{H2S_{ox}})</td>
<td>Maximum specific growth rate H(_2)S oxidation(^b)</td>
<td>d(^{3})</td>
<td>11</td>
</tr>
<tr>
<td>(\mu_{SOf})</td>
<td>Maximum specific growth rate (S^{0}_f) oxidation(^a)</td>
<td>d(^{3})</td>
<td>12</td>
</tr>
<tr>
<td>(z_{S})</td>
<td>Rate constant for (S^{0}_s) formation(^c)</td>
<td>d(^{-3})</td>
<td>13</td>
</tr>
<tr>
<td>(Y_{H2S})</td>
<td>Biological yield of H(_2)S oxidation(^a)</td>
<td>g SOB (g H(_2)S-S(^{-1}))</td>
<td>14</td>
</tr>
<tr>
<td>(Y_{SOf})</td>
<td>Biological yield of (S^{0}_f) oxidation(^a)</td>
<td>g SOB (g H(_2)S-S(^{-1}))</td>
<td>15</td>
</tr>
<tr>
<td>(Y_{SOs})</td>
<td>Biological yield of (S^{0}_s) oxidation(^a)</td>
<td>g SOB (g H(_2)S-S(^{-1}))</td>
<td>16</td>
</tr>
<tr>
<td>(K_{H2S_{ox}})</td>
<td>Half saturation constant for hydrogen sulfide(^c)</td>
<td>g H(_2)S-S m(^{-3})</td>
<td>17</td>
</tr>
<tr>
<td>(\alpha)</td>
<td>Temperature dependency constant(^a)</td>
<td>-</td>
<td>18</td>
</tr>
<tr>
<td>(\alpha_{pres})</td>
<td>Weighting factor for (S^{0}_f) oxidation(^c)</td>
<td>-</td>
<td>19</td>
</tr>
<tr>
<td>(K_{abs})</td>
<td>Switch constant for (S^{0}_f) oxidation(^c)</td>
<td>g H(_2)S-S m(^{-3})</td>
<td>20</td>
</tr>
<tr>
<td>(K_{SOf})</td>
<td>Switch constant for (S^{0}_f) oxidation(^c)</td>
<td>g S (g SOB(^{-1}))</td>
<td>21</td>
</tr>
<tr>
<td>(K_{SOs})</td>
<td>Switch constant for (S^{0}_s) oxidation(^a)</td>
<td>g S (g SOB(^{-1}))</td>
<td>22</td>
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<tr>
<td>(K_{SS})</td>
<td>Half saturation constant for oxygen(^a)</td>
<td>g O(_2) m(^{-3})</td>
<td>23</td>
</tr>
<tr>
<td>(K_{SOs})</td>
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<td>d(^{-1})</td>
<td>24</td>
</tr>
<tr>
<td>(K_{SS})</td>
<td>Half saturation constant for (S^{0}_s) oxidation(^a)</td>
<td>g S m(^{-3})</td>
<td>25</td>
</tr>
<tr>
<td>(b_{SOB})</td>
<td>Decay rate of (X_{SOB})(^a)</td>
<td>d(^{-1})</td>
<td>26</td>
</tr>
</tbody>
</table>

\(^a\) Estimated and not varied in the simulation

\(^b\) Obtained from Jensen et al. (2009; in press) and not varied in the simulation

\(^c\) Determined by model calibration

Vollertsen et al. 2011
RESULTS AND DISCUSSION
Parameter values on growth kinetics and stoichiometry were obtained from Jensen et al. (2009; in press). The model was then calibrated to measurements of immediate and delayed corrosion presented by Nielsen et al. (subm.b), who reported a dependency of the corrosion correction factor $k$ (Equation 1) on the H$_2$S surface loading as depicted in Figure 2 (measured data). The model was calibrated by optimizing model parameters as indicated in Table 1 with the result presented also in Figure 2. Oxygen was kept fixed at a non-limiting level.

The model application is exemplified on an intercepting sewer consisting of 1500 m of Ø 250 mm force main followed by 500 m of Ø 500 mm gravity sewer at 0.5% slope. At the discharge manhole of the force main there is a 0.5 m drop into the gravity sewer, causing intense H$_2$S release at this location. The average flow into the pump pit of the force main is 2 L s$^{-1}$, with daily maximum and minimum flows of 4.1 and 0.4 L s$^{-1}$, respectively. Wastewater composition corresponds to typical municipal sewage. Temperature is 15°C and pH is 7.4.

![Graphs showing H$_2$S concentration in bulk water and gas phase of gravity sewer at pH 7.4.](image)

**Figure 3.** Hydrogen sulfide in the bulk water and gas phase of the gravity sewer at pH 7.4.

Simulations were run for 20 days to ensure steady state conditions in the corrosion matrix. Figure 3 shows the simulated H$_2$S in the bulk water at different locations in the gravity main at day 20. The rapid variations in concentration are due to the intermittent operation of the pumps, while the slow variation in peak concentrations relate to the diurnal flow variation and the corresponding change in residence time in the force main. Figure 3 also shows the H$_2$S gas phase concentration of the first 20 m of the main. Close to the discharge manhole the gas phase concentration reaches 100 ppm, but already 20 m downstream, gas phase concentration has dropped to a maximum of 3 ppm. This corresponds to a H$_2$S removal rate in the gas phase of up to several ppm s$^{-1}$, in agreement with findings of Vollertsen et al. (2008a). At a lower bulk water pH, the H$_2$S release increases as the dissociation constant of H$_2$S is around 7.0. For
example at pH 6.4 – i.e. one pH unit lower than in the simulations of Figure 3 – the gas phase H₂S concentration at the discharge manhole peaks at 260 ppm and 20 m downstream the peaks still reach 20 ppm. At 50 m, gas phase concentrations drop to a few ppm (data not shown).

The corrosion rate corresponding to the simulations of Figure 3 is between 0.6 and 6 mm year⁻¹, with the highest rate closest to the discharge manhole. The corrosion is lowest around 20 m downstream of the force main discharge point, after which it slowly increases to 1.2 mm year⁻¹ some hundreds meter further downstream.

The accumulated corrosion during the simulations is shown in Figure 4. Free H₂S is present in the wastewater during the first 20 days, causing comparatively rapid corrosion. Here after precipitated of H₂S by iron salts is introduced, causing an absence of free H₂S in the gravity main. The simulations show that even though free H₂S is absent the corrosion continuous – albeit at a lower rate. This phenomenon is caused by an oxidation of elemental sulfur stored in the corrosion matrix, and is in agreement with findings by Nielsen et al. (subm.b). At a pH of 6.4 as mentioned above, the corrosion is approximately twice of what is at pH 7.4.

![Figure 4](image-url)

**Figure 4.** Delayed corrosion in the gravity main at pH 7.4 a various distances downstream of the force main discharge manhole. H₂S was absent from day 20 to 40

**CONCLUSION**

The today most commonly used concrete corrosion model was introduced by the US EPA in 1974, and the model is still a sound basis for corrosion prediction. However, it does not take dynamic conditions into account and is therefore best suited for predicting average corrosion rates. At hot-spots of hydrogen sulfide release it is crucial to predict the corrosion in greater detail, and for this purpose a model that includes important parts of the real dynamics in sewer systems has been introduced. A simulation example illustrates how such model can be applied to predict the complex behavior of hydrogen sulfide induced concrete corrosion.

The knowledge on in-sewer processes has progressed significantly since the US EPA model was developed 4 decades ago. It is the believe of the authors that the time now has come to introduce and test models which take the full dynamics of sewage flow, gas flow, mass...
transport, and biological as well as chemical processes into account. The perceived gain is a more detailed prediction of hydrogen sulfide and the related corrosion as well as better and more cost-effect hydrogen sulfide management.

REFERENCES