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Publication date:
2009

Document Version
Publisher's PDF, also known as Version of record

[Link to publication from Aalborg University](#)

Citation for published version (APA):
Jensen, H. S. (2009). *Hydrogen sulfide induced concrete corrosion of sewer networks* (1. ed.). Institut for Kemi, Miljø og Bioteknologi, Aalborg Universitet.

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Hydrogen sulfide induced concrete corrosion of sewer networks

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Ph.D. Dissertation, 2009

Printed in Denmark by
UNIPRINT, Aalborg University, May 2009
ISBN 978-87-90033-58-3
ISSN 0909-6159

Cover design: Hanne Rimmen

Preface

This dissertation is submitted in partial fulfillment of the requirements for obtaining the Doctor of Philosophy (Ph.D.) degree. The dissertation consists of an extended summary and nine supporting papers. The main results of the Ph.D. study are presented in the extended summary and additional details are given in the supporting papers. When the supporting papers are referred in the text, the reference is marked with a roman numeral corresponding to the number of the paper in the list of supporting papers.

The study was carried out under the supervision of Associate Professor Jes Vollertsen and Associate Professor Asbjørn Haaning Nielsen at the Section of Environmental Engineering, Department of Biotechnology, Chemistry and Environmental Engineering, Aalborg University, Denmark. A part of the study was conducted in collaboration with Dr. Ir. Piet Lens at the Sub-department of Environmental Technology, Agricultural University of Wageningen, the Netherlands. The study was completed during the period September 2005 to November 2008 and was funded by The Danish Technical Research Council.

At this point there are a lot of people to thank. Thank you Jes, Asbjørn and Thorkild for good discussions both the scientific and the not so scientific. The same to all my office mates: Anja, Annette, Aviaja, Christel, Elise, Heidi, Martijn, Pim, Poul, Sharul, Søren and Tove. And to all the people at I18: thanks for being great colleagues.

Also a special thank to Piet Lens and the people at Environmental Technology in Wageningen for valuable help and good company during my stay in the Netherlands and to Laura also for the “Scandinavian community”.

But most of all, I want to thank my crazy, wonderful family for always being there, whenever I need them!

Aalborg, November 2008

Henriette Stokbro Jensen

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English abstract

When wastewater is transported in sewer networks, hydrogen sulfide can be formed under certain circumstances. Hydrogen sulfide is a malodorous gas, which furthermore is toxic, also in the concentrations that can be found in sewers. This therefore causes safety problems for sewer workmen, but also odor nuisances for the people living close to sewer systems. An additional problem caused by hydrogen sulfide is corrosion of concrete surfaces. This is due to hydrogen sulfide being oxidized to sulfuric acid on concrete surfaces, which is comprised of alkaline materials, that forms gypsum when they come in contact with acid.

This study has focused on the processes taking place at the concrete surfaces, when they are exposed to hydrogen sulfide. The purpose of this has been to determine the kinetics and stoichiometry of the processes that are governing for the uptake of hydrogen sulfide on the surfaces and the processes involved in the further oxidation of hydrogen sulfide to sulfuric acid. This knowledge can be applied to improve the existing tools for predicting the distribution of hydrogen sulfide in sewer networks as well as the risk of concrete corrosion. The investigations have primarily been based on samples of concrete corrosion products, sampled on heavily corroded concrete surfaces. Additionally measurements have been performed in a pilot scale setup, simulating the conditions in a gravity sewer pipe.

The results have shown, that the oxidation of hydrogen sulfide on corroded concrete surfaces is primarily biological, however, adsorption of hydrogen sulfide does influence the actual uptake of hydrogen sulfide on the surfaces. The uptake of hydrogen sulfide on the concrete surfaces could be described with n^{th} order kinetics and the process was fast in comparison with the release of hydrogen sulfide from the wastewater. This means that the uptake of hydrogen sulfide on the concrete surfaces is significant for the distribution of hydrogen sulfide in the sewer atmosphere.

The biological oxidation of hydrogen sulfide within the corrosion products developing on the concrete surfaces could be described by saturation kinetics, and elemental sulfur was identified as an intermediate product in the oxidation. Some results indicated that the elemental sulfur could be transformed from a readily biodegradable form to an almost inert form which hence would not contribute significantly to the corrosion process. It is, however, at this point not clear under which circumstances this slowly degradable form of sulfur is formed. A survival study showed that the bacteria were viable even after 6 to 12 months of hydrogen sulfide starvation, and it is possible that the slowly biodegradable sulfur acted as substrate for the bacteria in this period.

The oxidation kinetics of hydrogen sulfide was combined with the existing WATS (Wastewater Aerobic-anaerobic Transformations in Sewers) model concept. This model concept is applied to simulate processes taking place in wastewater during transport in sewer networks. The combined model was applied to predict corrosion rates in a simple gravity sewer pipe downstream of a force main. The results of the model emphasized the active hydrogen sulfide oxidizing biomass as a key parameter in the prediction of corrosion rates. Furthermore it was found, that slowly biodegradable elemental sulfur comprised up to 70% of the entire sulfur pool in the corrosion products. This means that an assumption that all hydrogen sulfide supplied to the concrete surfaces contributes to the corrosion may lead to overestimation of the corrosion rate.

This study has contributed to an increased understanding of the oxidation pathway of hydrogen sulfide on corroding concrete surfaces, and hence of an important part of the sulfur cycle in sewers. This knowledge can be applied in future predictions of hydrogen sulfide buildup and transformations in sewer networks.

Dansk resume

Svovlbrinte kan dannes i spildevand, når dette transporteres i afløbssystemer. Svovlbrinte er en ildelugtende gas, der ydermere er giftig selv i koncentrationer, der ikke er urealistisk høje for kloaksystemer. Det kan derfor give anledning til sikkerhedsproblemer for kloakarbejdere samt lugtproblemer for borgerne ved udsatte steder af kloaksystemet. Ud over disse problemer forårsager svovlbrinte også korrosion, når det kommer i kontakt med betonoverflader. Dette skyldes, at svovlbrinte oxideres til svovlsyre på betonoverfladen, og da bindemidlet i beton er basisk, forvitres dette til gips, når det udsættes for syre.

I dette studium har fokus været på de processer, der finder sted på betonoverflader, når de udsættes for svovlbrinte. Formålet med dette har været at bestemme kinetik og støkiometri for de processer, der er styrende for optaget af svovlbrinte på overfladerne, samt for den videre oxidation til svovlsyre. Denne viden kan i fremtiden udnyttes til at forbedre de eksisterende redskaber til forudsigelse af svovlbrinteudbredelsen i kloaksystemer samt af risikoen for betonkorrosion. Undersøgelserne har primært taget udgangspunkt i prøver af korrosionsprodukter, udtaget på stærkt korroderede overflader. Derudover har der været foretaget undersøgelser i et pilotskalaanlæg, der simulerer forholdene i en gravitationsledning i et afløbssystem.

Resultaterne viste, at oxidationen af svovlbrinte på korroderede betonoverflader var overvejende biologisk, dog havde sorption af svovlbrinte også betydning for selve optaget af svovlbrinte på overfladerne. Optaget af svovlbrinte på betonoverfladerne kunne beskrives med n 'te ordens kinetik og processen var hurtig i forhold til frigivelse af svovlbrinte fra spildevandet. Det betyder, at optaget af svovlbrinte er vigtig som begrænsende faktor for udbredelsen af svovlbrinte i kloaksystemer.

Den biologiske oxidation af svovlbrinte kunne beskrives med mætningskinetik og elementært svovl blev fundet som mellemprodukt i oxidationen. Nogle resultater indikerede, at det elementære svovl kunne omdannes til en næsten inert pulje af elementært svovl, som dermed ikke bidrager til korrosionen. Det er dog ikke klarlagt hvilke omstændigheder, der fører til dannelsen af dette svært omsættelige svovl. Overlevelseshversøg viste, at bakterierne kunne overleve uden svovlbrinte i mellem seks og 12 måneder. Bakterierne bruger muligvis den sværtomsættelige svovlpulje som substrat i sådanne perioder uden svovlbrintetilførsel.

Oxidationskinetikken for svovlbrinte blev kombineret med det eksisterende WATS-modelkoncept. WATS-modellen bruges til modellering af processer i spildevand under transport i afløbssystemer. Den samlede model blev brugt til forudsigelse af korrosionsrater i en simpel gravitationsledning nedstrøms en trykledning. Modelleringen understregede den aktive biomasse som en nøgleparameter i forudsigelsen af korrosionsraten. Det blev ligeledes fundet ved modelleringen, at det sværtomsættelige svovl udgjorde op til 70% af den samlede svovlpulje på betonoverfladen. Det betyder, at en antagelse om, at alt det svovlbrinte, der tilføres fra spildevandet til betonoverfladerne, også bidrager til korrosionen, kan føre til overvurdering af korrosionsraten.

Dette studium har bidraget til større forståelse af oxidationsvejen for svovl på korroderede betonoverflader og dermed af en vigtig del af svovlkredsløbet i kloakker. Denne viden vil kunne anvendes i forbindelse med forudsigelse af svovlbrinteophobning i afløbssystemer.

1 Introduction and Objective

Corrosion of concrete caused by hydrogen sulfide has been recognized as a serious problem in collection systems for the past century (Olmsted and Hamlin, 1900; Parker, 1947; Okabe *et al.*, 2007). The problem of hydrogen sulfide induced concrete corrosion is known in collection systems in most of the world (Zhang *et al.*, 2008). In some of the worst cases, the lifetime of sewer pipes and pumping stations has been reduced to less than ten years (Hvitved-Jacobsen, 2002; Olmsted and Hamlin, 1900). Besides the costs of restoration, the costs of preventive measures should also be considered when estimating the economic impact of hydrogen sulfide related problems (Sydney *et al.*, 1996).

Besides the problem of concrete corrosion, the presence of hydrogen sulfide in collection systems also causes other problems which are of major concern. Hydrogen sulfide is a nerve gas and is toxic in the concentration ranges that can occur in sewers (Hvitved-Jacobsen, 2002). It is therefore an important safety concern for sewer workers (Christia-Lotter *et al.*, 2007). A third problem associated with hydrogen sulfide is odor nuisances. Odor problems from wastewater collection systems are of increasing concern in the management of these installations. Hydrogen sulfide has a characteristic smell often associated with the smell of rotten eggs. Hydrogen sulfide is not the only odorous gas in sewer networks, however, as hydrogen sulfide is easy to measure, it is also often used as marker for sewer odor, although other compounds also contribute to the odor (Hwang *et al.*, 1995).

With respect to these problems, the mechanisms of hydrogen sulfide induced concrete corrosion are also important, as the process causes removal of hydrogen sulfide on the pipe surfaces. This is an important part of the sulfur mass balance in sewers. The concrete corrosion process leads to removal of hydrogen sulfide from the sewer atmosphere and it has therefore potentially a positive effect on odor and safety problems.

The objective of this Ph.D. study was to improve the conceptual understanding of the processes involved in hydrogen sulfide induced concrete corrosion of sewer networks. This should lead to improved possibilities for prediction of corrosion problems. In the achievement of this objective, experiments have been conducted to determine the mechanisms and kinetics of the uptake of hydrogen sulfide on the concrete surfaces, as well as determine reaction pathways and kinetics of the hydrogen sulfide oxidation within the corroded concrete.

2 Sulfur pathways in wastewater

Sulfur is an abundant and versatile element in sewers and many reaction pathways exist for compounds containing sulfur. An overview of the main reactions is given in Figure 2.1:

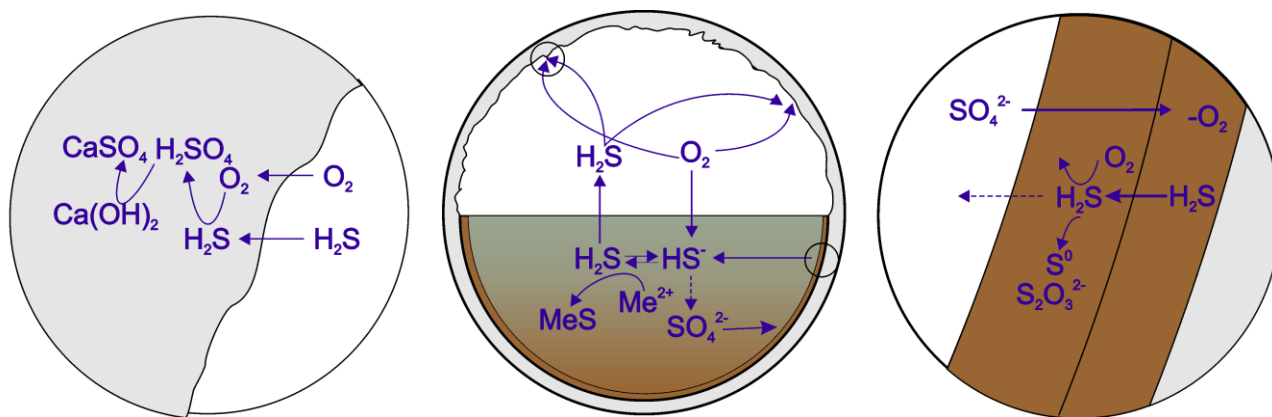


Figure 2.1. Reaction pathways for sulfur in sewers.

2.1 Sulfide production

Sulfide in sewers is formed when sulfate reducing bacteria oxidize organic matter with sulfate or other oxidized sulfur components as electron acceptor. The process takes place under anaerobic conditions, e.g. when neither oxygen nor nitrate is present and is mainly ascribed to the activity of bacteria of the genus *Desulfovibrio* and *Desulfobulbus* (USEPA, 1985; Okabe *et al.*, 1999). The process is primarily associated with sewer biofilms and sediments as the bacteria are slow growing and hence washed out of the bulk water phase (Hvitved-Jacobsen, 2002; Kitagawa *et al.*, 1998) (Figure 2.1, right hand side). The anaerobic nature of the process means that in gravity sewers, hydrogen sulfide production mainly takes place at temperatures above 15-20 °C and at slow flow ($< 30 \text{ cm s}^{-1}$) (Hvitved-Jacobsen and Nielsen, 2000). The high temperatures increases biological activity thereby increases both the consumption of oxygen and the production of sulfide. The slow flow limits turbulence, hereby suppressing the reaeration of the wastewater and facilitates the production of thicker biofilms (Hvitved-Jacobsen and Nielsen, 2000). An opposing effect of slow flowing wastewater is that the thickness of the diffusive boundary layer above the biofilms increases. This can limit the supply of organic matter and nutrients to the biofilm hence limiting the sulfide production (USEPA, 1985). In force mains, the sulfide production can take place at lower temperatures, provided that the anaerobic retention time is sufficient e. g. exceeds 0.5 – 2 hours (Hvitved-Jacobsen and Nielsen, 2000; Hvitved-Jacobsen, 2002). This means that in countries with temperate climate, like Denmark, hydrogen sulfide problems are often associated with the discharge from force mains (Hvitved-Jacobsen, 2002).

2.2 Sulfide oxidation and precipitation

Sulfide can be produced in the anaerobic parts of biofilms that is partly penetrated by oxygen. In this case, oxidation of sulfide takes place in the parts of the biofilms containing oxygen and nitrate, leading to an internal cycle of sulfur within the biofilms (Figure 2.1, right hand side) (Kühl and Jørgensen, 1992; Okabe *et al.*, 2005). The bacteria *Thiothrix*, *Thiobacillus denitrificans* and

Thiomicrospira denitrificans have been identified in sulfide oxidizing biofilms (Okabe *et al.*, 2005). In order for the sulfide formed in sewer biofilms to be released to the bulk wastewater, the concentration of dissolved oxygen (DO) in the wastewater needs to be lower than 1 to 0.1 g O₂ m⁻³, depending on the temperature and flow conditions (USEPA, 1985; ASCE, 1989).

Sulfide supplied to an aerobic sewer biofilm from the wastewater has also been shown to be oxidized by the biofilm (Nielsen *et al.*, 2005). Such a scenario may be found in a gravity sewer downstream of a force main. Both when sulfide is cycled internally in the biofilm and when it is supplied from the wastewater, studies suggest that elemental sulfur is an intermediate product in the oxidation of sulfide to sulfate (Nielsen *et al.*, 2005; Okabe *et al.*, 2005).

When sulfide is present in aerobic wastewater or anoxic wastewater, sulfide is removed from the wastewater by oxidation (Figure 2.1, middle). The oxidation of sulfide with nitrate has been found to be a biological process (Yang *et al.*, 2005) whereas the oxidation of sulfide with oxygen occurs both chemically and biologically (Nielsen *et al.*, 2006a). The main products in the chemical sulfide oxidation are thiosulfate and sulfate, whereas elemental sulfur is formed in the biological oxidation (Nielsen *et al.*, 2006a; Okabe *et al.*, 2005). Using modeling, Nielsen *et al.* (2006b) found that in a gravity sewer downstream of a force main, sulfide oxidation in the biofilm and biological sulfide oxidation in the wastewater was in general the main processes responsible for the removal of sulfide from the wastewater (Nielsen *et al.*, 2006b).

Besides the oxidation processes, sulfide can be removed in the wastewater by precipitation with metals (Figure 2.1, middle). Several metals form precipitates with sulfide. The precipitation appears to be most efficient when the pH of the solution is between 8 and 10, hence high compared to normal wastewater pH (Kim *et al.*, 2002; Henze, 1997). The metal concentration in Danish domestic wastewater is in the order of magnitude of < 5 g m⁻³ with aluminum, iron and zinc as the most common metals (Henze, 1997). Besides resulting in precipitation, iron catalyzes the chemical sulfide oxidation in aerobic wastewater, which may be of higher importance for the sulfide removal than precipitation by iron (Nielsen *et al.*, 2007).

2.3 Release of hydrogen sulfide to the sewer atmosphere

Emission of hydrogen sulfide from the wastewater to the sewer atmosphere is an important process because the problems with hydrogen sulfide in sewers mainly are associated with gaseous hydrogen sulfide. Hydrogen sulfide is a weak acid with a dissociation constant of 7.0 (20°C) and it is only the non-dissociated form which can be emitted to the sewer atmosphere. The pH of the wastewater is therefore of importance when evaluating the potential hydrogen sulfide emission (Yongsiri *et al.*, 2004a). Figure 2.2 shows an example from a field investigation, where the concentration of hydrogen sulfide in a sewer atmosphere increases as the pH of the wastewater decreases (Nielsen *et al.*, 2008 (I)).

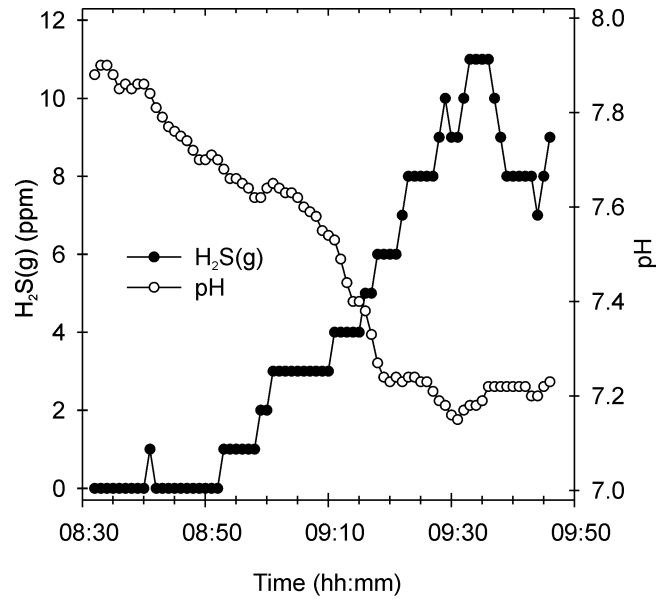


Figure 2.2. Wastewater pH and hydrogen sulfide gas phase concentration in a sewer manhole (Nielsen *et al.*, 2008 (I)).

In Denmark, the public water supply is in many areas based on groundwater extracted from limestone aquifers. This usually results in wastewaters that are slightly alkaline and have a stable pH due to a high buffer capacity.

The turbulence of the wastewater is also important for the emission of hydrogen sulfide to the sewer atmosphere as increased turbulence leads to increased emission (Yongsiri *et al.*, 2004a). This means that certain sewer structures such as drops, increased elevation, sharp bends and force main discharge structures can increase the emission of hydrogen sulfide and hence increase the risk of concrete corrosion (ASCE, 1989).

The temperature affects the hydrogen sulfide emission so that increasing temperature leads to higher emission rate. Additionally the temperature affects the acid dissociation constant for hydrogen sulfide (Yongsiri *et al.*, 2004b).

3 Removal of hydrogen sulfide from the sewer atmosphere

When hydrogen sulfide in the sewer atmosphere comes into contact with the pipe surface, sorption will take place. Studies concerned with the behavior of hydrogen sulfide in sewer atmospheres have shown that the sorption on the pipe surfaces is important for the concentration of hydrogen sulfide in the atmosphere (Nielsen *et al.*, 2008 (I); Matos and Aires (1995)).

3.1 Pilot scale setup for the study of hydrogen sulfide in the sewer atmosphere

The removal of hydrogen sulfide from the sewer atmosphere has been studied in a pilot scale setup. The pilot scale setup consisted of eight reactors. Each reactor simulated a gravity sewer pipe section. Six of the reactors consisted of concrete pipe segments (Figure 3.1A), one reactor consisted of PVC pipe segments and the last reactor of HDPE segments (Figure 3.1B) (Vollertsen *et al.*, 2008 (II); Nielsen *et al.*, 2008 (III)). The concrete reactors were designated with roman numerals, I through VI and each reactor consisted of 10 pipe segments designated with letters, a through j (Figure 3.1A). The plastic reactors each consisted of two pipe segments and the reactors were designated PVC and HDPE, respectively.

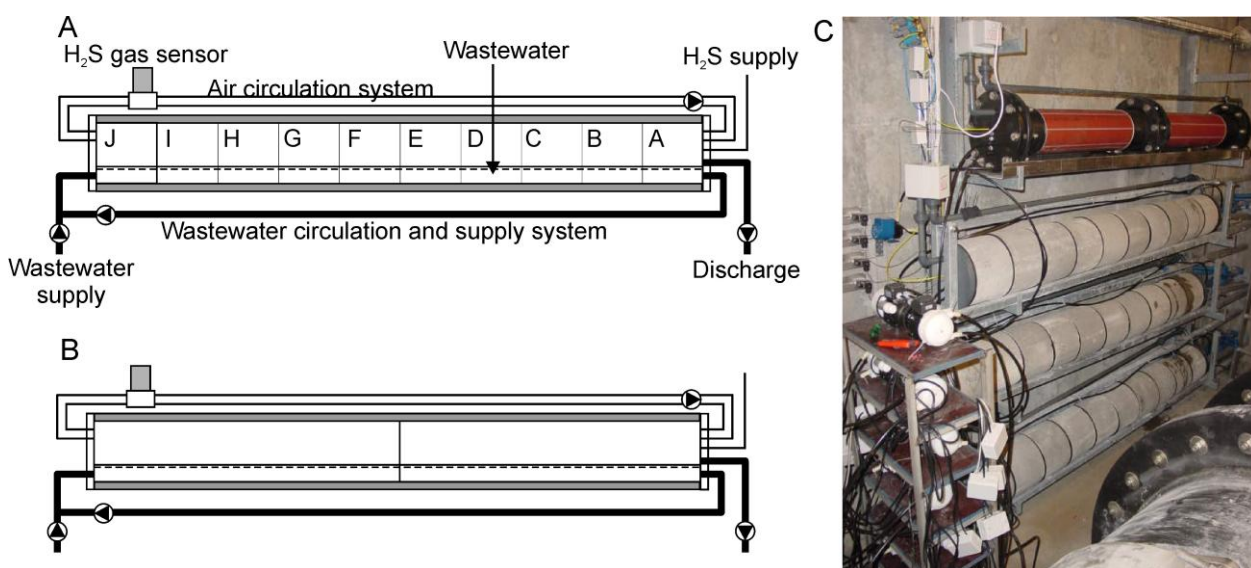


Figure 3.1. A: Outline of one of the concrete reactors. B: Outline of the PVC reactor and the HDPE reactor (explanations similar to those of figure 3.1A). C: Photo showing half the setup i.e. three concrete reactors and the HDPE reactor.

Wastewater was circulated in the pipes at a flow rate of approximately 0.1 l s^{-1} and fresh wastewater was supplied every 2nd hour. The sewer gas phase was likewise cycled through the reactors by means of a blower at a velocity of 0.053 m s^{-1} .

The configuration of the reactors is presented in Table 3.1. Hydrogen sulfide was injected directly into the sewer atmosphere of each reactor to an initial concentration in the gas phase of approximately 1000 ppm. Hydrogen sulfide was supplied from a flask containing compressed hydrogen sulfide (Yara Praxair, Fredericia, Denmark). The concentration of hydrogen sulfide was

measured in the air circulation system using OdalogTM hydrogen sulfide gas sensors (App-Tek International Pty Ltd, Brendale, Australia).

The entire setup was placed in a sewer monitoring station in the town of Frejlev, Denmark. The reactors were supplied with wastewater from the Frejlev sewer system. This catchment is purely residential and has approximately 2000 inhabitants.

Prior to the measurements, the reactors had a run-in period, where hydrogen sulfide was injected into the concrete reactors at fixed time intervals. The frequency of the injections was adapted to the rate of the hydrogen sulfide sorption to ensure that unrealistic high hydrogen sulfide concentrations did not build up in the reactors. The measurements were initiated when the concrete reactors showed clear signs of initiating corrosion. Further details can be found in Vollertsen *et al.* (2008 (II)) and Nielsen *et al.* (2008 (III)).

Table 3.1. Main characteristics of the pilot scale test reactors (Nielsen *et al.*, 2008 (III)).

	Concrete	HDPE	PVC
Inner diameter of reaction chamber [m]	0.200	0.184	0.188
Water depth [m]	0.050	0.041	0.041
Gas volume [m ³]	0.051	0.044	0.047
Wastewater volume [m ³]	0.012	0.009	0.009
Surface area of the reaction chamber exposed to the gas phase [m ²]	0.838	0.794	0.816
Surface area of air circulation system [m ²]	0.207	0.207	0.207

3.2 Simulation of hydrogen sulfide removal measurements

The hydrogen sulfide oxidation rate was determined as the slope of the measured hydrogen sulfide concentration versus time. This treatment of the concentration measurements are illustrated in Figure 3.2.

The kinetics of the hydrogen sulfide surface removal were determined using n^{th} order kinetics (Equation 1).

$$\frac{dp_{H_2S}}{dt} = k_n p_{H_2S}^n \quad (1)$$

Where p_{H_2S} is the partial pressure of hydrogen sulfide gas [ppm], t is the time [h], k_n is the gas phase removal rate constant [ppm¹⁻ⁿ h⁻¹] and n is the reaction order [-].

Applying the ideal gas law, a surface-specific hydrogen sulfide removal rate was calculated for the concrete reactors (Equation 2).

$$F_{H_2S} = \frac{p_{atm} M_S V_{gas} 10^{-6}}{R_{gas} T_{abs} A_{conc}} k_n p_{H_2S}^n = k_F p_{H_2S}^n \quad (2)$$

Where F_{H_2S} is the surface-specific hydrogen sulfide removal rate [g S m⁻² h⁻¹], p_{atm} is the atmospheric pressure [Pa], M_S is the molar mass of sulfur [g mole⁻¹], V_{gas} is the total gas phase

volume in the reactor [m^3], R_{gas} is the universal gas constant [$\text{J K}^{-1} \text{mole}^{-1}$], T_{abs} is the absolute temperature [K], A_{conc} is the concrete surface subject to sewer gas [m^2] and k_F is the surface-specific process rate constant [$\text{g S m}^{-2} \text{h}^{-1} (\text{ppm H}_2\text{S})^{-n}$].

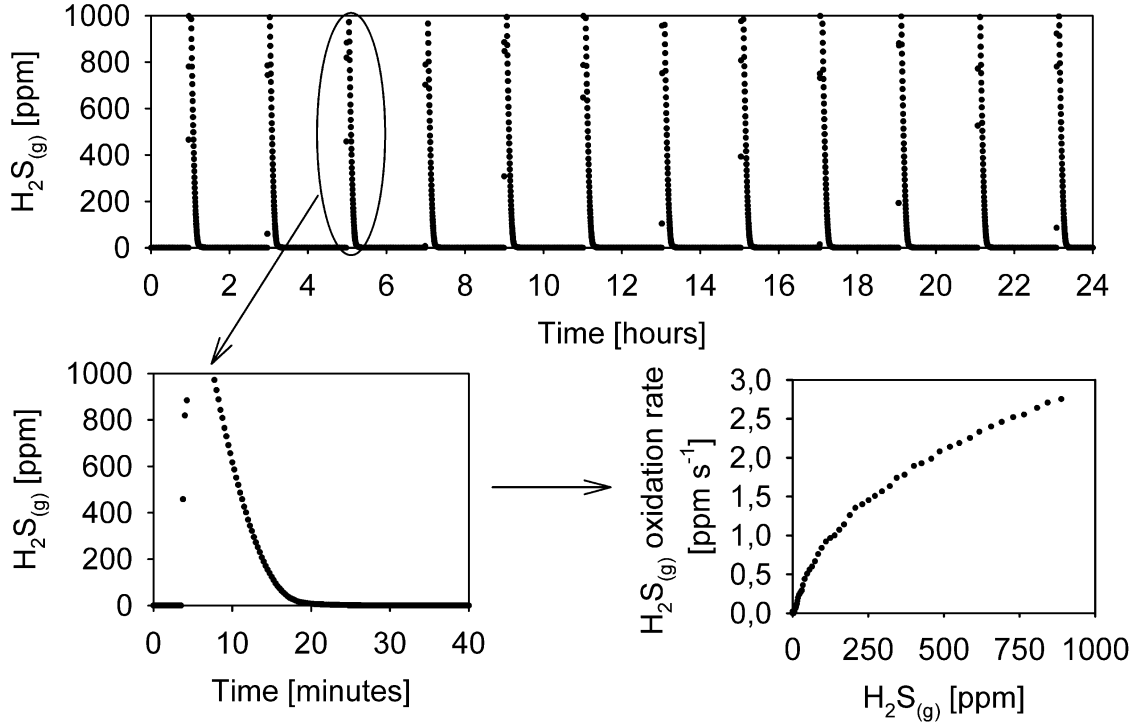


Figure 3.2. Principle of the measurements of the removal of hydrogen sulfide from the gas phase exemplified with data from a concrete reactor (Vollertsen *et al.*, 2008 (II)).

The data from the plastic reactors were corrected for the loss of hydrogen sulfide to the wastewater in the reactor (Equation 3). Due to the comparatively high surface removal rate, this loss was negligible for the concrete reactors (Vollertsen *et al.*, 2008 (II)).

$$\frac{p_{H_2S}}{dt} = K_L \frac{A_w}{V_{gas}} \frac{R_{gas} T_{abs}}{M_S p_{atm}} 10^6 \left(C_{H_2S,Eq} - C_{H_2S} \right) + k_n p_{H_2S}^n \quad (3)$$

Where K_L is the mass transfer coefficient [m h^{-1}], A_w is the surface area of the wastewater [m^2], $C_{H_2S,Eq}$ is the dissolved hydrogen sulfide concentration of the wastewater at equilibrium with the gas phase [g S m^{-3}] and C_{H_2S} is the actual concentration of hydrogen sulfide in the wastewater at the specific pH [g S m^{-3}].

When necessary, the rates were temperature corrected using an Arrhenius-type equation with a temperature coefficient of 1.03, typical for diffusion limited processes (Hvitved-Jacobsen, 2002).

Due to the changing reaction order, comparison between the experiments could not be made by comparing the different values obtained for k_n . Therefore the removal rates at hydrogen sulfide concentration of 10, 100 and 1000 ppm were calculated. These were designated r_{10} , r_{100} and r_{1000} , respectively.

3.3 Developments in the hydrogen sulfide removal kinetics

The first measurements of the hydrogen sulfide removal kinetics for the concrete reactors were initiated approximately 3 months after the startup of the pilot scale setup. When these first measurements were done, the concrete surface within the reactors showed clear signs of initiated corrosion, however, not the entire surface was visibly attacked (Figure 3.3A) (Vollertsen *et al.*, 2008 (II)).

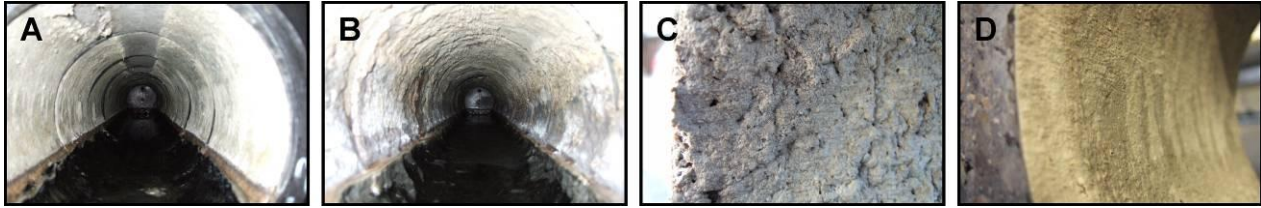


Figure 3.3. A: Slightly corroded concrete pipe. The visible corrosion has not reached the pipe crown. B: Heavily corroded concrete pipe. C and D: close up photo of corroded surfaces.

One month later, the entire concrete surface was attacked by visible corrosion (Figure 3.3B). During this first month of measurements a trend towards increasing hydrogen sulfide removal rate could be measured (Figure 3.4). Here after no systematic change in the hydrogen sulfide removal rate could be observed. The changes could not be explained by changes in temperature.

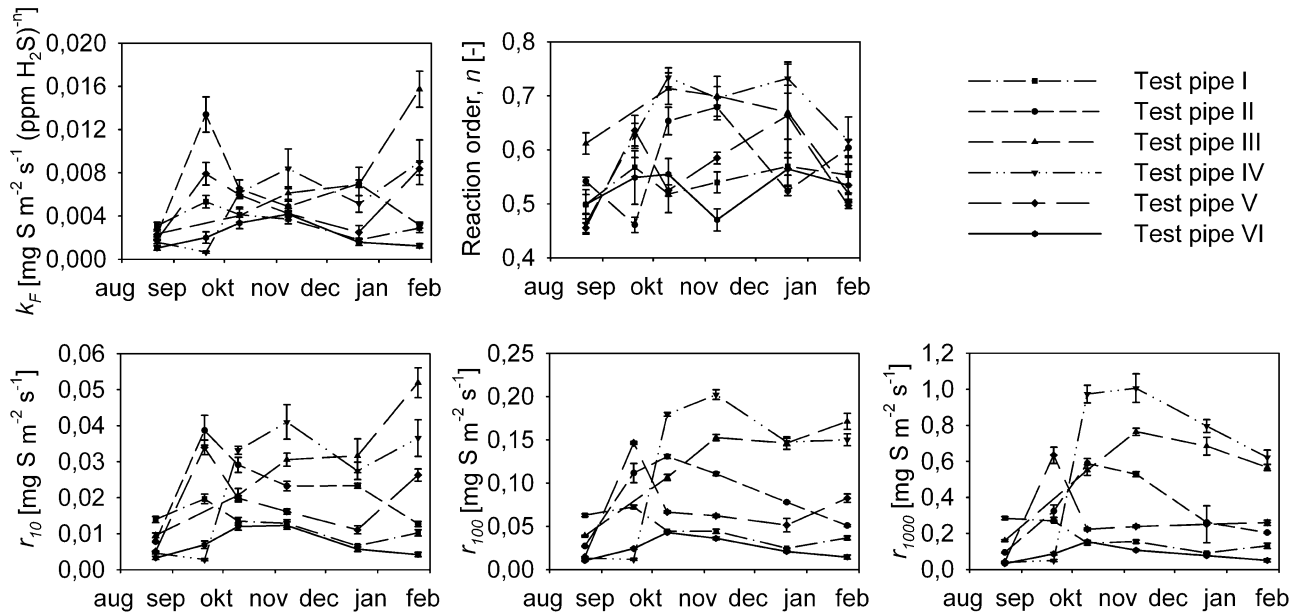


Figure 3.4. Development in the kinetic parameters for the hydrogen sulfide removal from the sewer gas phase for the concrete reactors. The parameters are not temperature corrected (Vollertsen *et al.*, 2008 (II)).

The removal rates were of the same order of magnitude as those reported for hydrogen sulfide oxidation by submerged sewer biofilms by Nielsen *et al.* (2005). Compared to the release rate of hydrogen sulfide from the sewer bulk water to the sewer atmosphere, the removal rates of hydrogen sulfide on the concrete surface were fast. The immediate consequence of this is that the hydrogen

sulfide release rates controls the corrosion rate and that corrosion can occur at low concentrations of hydrogen sulfide in the sewer atmosphere (Vollertsen *et al.*, 2008 (II)).

After approximately 18 months of operation, the corrosion products were washed off the concrete pipe segments to investigate the effects of flushing of the pipes. The removal of the corrosion products resulted in an immediate reduction of the surface removal rate. The removal rate did however increase again, particularly during the first 10 – 12 days after washing. After 30 – 40 days the removal rate reached a level similar to the level before the washing (Nielsen *et al.*, 2008 (III)). The fast regeneration of the hydrogen sulfide removal rate is in accordance with the findings of Islander *et al.* (1991). These findings showed that flushing of the concrete pipes which removes the corrosion products is only likely to have a short term effect on the corrosion process.

3.4 Effect of pipe material on the removal of hydrogen sulfide from the sewer atmosphere

The effect of the pipe material on the removal of hydrogen sulfide from the sewer atmosphere was investigated by comparing r_{10} , r_{100} and r_{1000} for the three types of reactors (Figure 3.4). The removal rates on the concrete surfaces were approximately two orders of magnitude higher than those of the plastic surfaces, whereas the difference between the two types of plastic was not significant (Nielsen *et al.*, 2008 (III)).

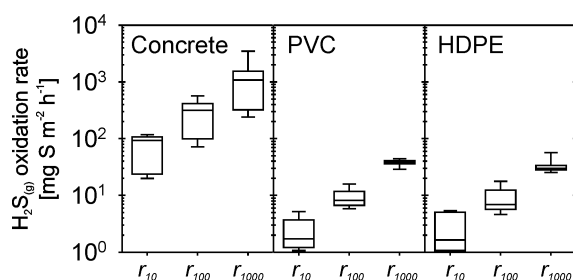


Figure 3.5. Box-plot of the hydrogen sulfide removal rates of concrete, PVC and HDPE pipe reactors after 16 months of operation. Data are corrected to 15°C (Nielsen *et al.*, 2008 (III)).

These results are of special interest for odor problems from sewers. Hydrogen sulfide is often used as marker for odorous substances in sewers as it is relatively easy to measure compared to other odorous substances (Gostelow and Parsons, 2001). Hydrogen sulfide is not necessarily an appropriate measure of sewer odor as other odorous compounds may have other properties with respect to release from the wastewater and especially degradation on the pipe surfaces (Vollertsen *et al.*, 2008 (IV)). The results displayed in Figure 3.5 indicate that hydrogen sulfide is possibly a better measure for odorous substances in sewers made of plastic materials than in concrete sewers.

4 Fate of hydrogen sulfide in the corroded concrete matrix

When hydrogen sulfide is taken up by the concrete pipe surface it is oxidized to sulfuric acid. The acid reacts with the alkaline components of the concrete, mainly calcium hydroxide and calcium carbonate. The product of this reaction is mainly gypsum, which has little structural strength for which reason the concrete pipe is weakened (Lea and Desch, 1935; Parker, 1945b). The oxidation of hydrogen sulfide on the pipe surface is biological after the pH of the surface has dropped below approximately 8-9 (Parker, 1947; Okabe *et al.*, 2007).

Investigating the corrosion products from heavily corroded pipes, the fate of hydrogen sulfide within the corroded concrete matrix was studied. In this way it was attempted to gain more information on the important mechanisms in the uptake of hydrogen sulfide on the corroded concrete surface. The focal point was to determine the kinetics and stoichiometry of the hydrogen sulfide oxidation.

4.1 Background

The corrosion products on heavily corroded concrete surfaces form a porous matrix. The visual impression of corroded concrete surfaces can vary as illustrated in Figure 3.3. The solids in the matrix consist mainly of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and quartz. The quartz originates from the sand and small stones in the concrete whereas gypsum is formed in the corrosion process (Tazaki *et al.*, 1992; De Graef *et al.*, 2005). Jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$) and ettringite ($\text{Ca}_4\text{Al}_2(\text{SO}_4)(\text{OH}) \cdot 2\text{H}_2\text{O}$) have also been identified as components in the corrosion products (Tazaki *et al.*, 1992; Davis *et al.*, 1998; Mori *et al.*, 1992).

The dry matter content of the corrosion products of the present studies was between 65% and 84% of which the weight loss after ignition at 550°C was 2% to 2.7%, i.e. the inorganic materials were the main constituents of the corrosion products (Nielsen *et al.*, 2008 (III); Jensen *et al.*, in press (V)). The median pore water pH of corrosion products sampled in a sewer manhole was 0.5 (Jensen *et al.*, in press (V)). Okabe *et al.*, (2007) finds that a pH between 2 and 3 in the outermost 2 mm of corrosion products and both Parker (1945b) and Mori *et al.*, (1992) reports findings of pH values below 2 in heavily corroded concrete.

Microbial analysis of concrete corrosion products was first reported in 1945 by Parker (1945a; 1945b). Parker (1945b) also demonstrated that the concrete corrosion did not take place under sterile conditions. Several other microbial studies have followed. The majority of the studies have been based on cultivation methods (e.g. Parker 1945a; Parker and Prisk, 1953; Milde *et al.*, 1983). Later also molecular microbiological methods have been applied to the corrosion products to reveal the microorganisms present (e.g. Okabe *et al.*, 2007; Vincke *et al.*, 2001). Table 4.1 summarizes the bacteria found in heavily corroded concrete matrices. It is widely agreed that the most abundant bacteria species when the pH of the concrete surface is lower than 2 is *Acidithiobacillus thiooxidans* (formerly *Thiobacillus concretivorus* and *Thiobacillus thiooxidans* (Kelly and Wood, 2000)) and this result is consistent for both the studies using cultivation techniques and those using molecular techniques (e.g. Okabe *et al.*, 2007; Parker, 1945a; Hernandez *et al.*, 2002). The roles of the other bacteria on the heavily corroded concrete surfaces are largely unknown. At surface pH between 2 and 8-9 a succession of sulfur oxidizing microorganisms is reported to take place on the concrete surface (Parker, 1947; Okabe *et al.*, 2007; Islander *et al.*, 1991). As the focus of this study has been

the heavily corroded concrete where *Acidithiobacillus thiooxidans* is the dominant species, this succession will not be dealt with further.

Table 4.1. Microorganisms identified in heavily corroded concrete.

Genus	Species	References
<i>Achromobacter</i>	<i>xylosoxidans</i>	Okabe <i>et al.</i> , 2007
<i>Acidiphilium</i>	<i>acidophilum</i>	Nica <i>et al.</i> , 2000 Okabe <i>et al.</i> , 2007 e.g. Nica <i>et al.</i> , 2000,
<i>Acidithiobacillus</i>	<i>thiooxidans</i>	Vincke <i>et al.</i> , 2001, Hernandez <i>et al.</i> , 2002 Okabe <i>et al.</i> , 2007
<i>Acinetobacter</i>	<i>junii</i>	Okabe <i>et al.</i> , 2007
<i>Aeromicrobium</i>	<i>erythreum</i>	Vincke <i>et al.</i> , 2001
<i>Agrobacterium</i>		Vincke <i>et al.</i> , 2001
<i>Azonexus</i>	<i>caeni</i>	Okabe <i>et al.</i> , 2007
<i>Bacillus</i>	<i>psychrodurans</i>	Vincke <i>et al.</i> , 2001
<i>Cellvibrio</i>		Vincke <i>et al.</i> , 2001
<i>Clostridium</i>	<i>bartletti</i>	Okabe <i>et al.</i> , 2007
<i>Flavobacterium</i>	<i>aff.</i>	Vincke <i>et al.</i> , 2001
<i>Leptospirillum</i>	<i>ferrooxidans</i>	Okabe <i>et al.</i> , 2007
<i>Methylobacterium</i>		Vincke <i>et al.</i> , 2001
<i>Microbacterium</i>		Nica <i>et al.</i> , 2000
<i>Mycobacterium</i>	<i>sydneyensis</i>	Vincke <i>et al.</i> , 2001
	<i>florentinum</i>	Okabe <i>et al.</i> , 2007
<i>Ochrobactrum</i>	<i>antrophii</i>	Nica <i>et al.</i> , 2000
	<i>tritici</i>	Okabe <i>et al.</i> , 2007
<i>Propionibacterium</i>	<i>acnes</i>	Vincke <i>et al.</i> , 2001
<i>Pseudomonas</i>	<i>pseudoalcaligenes</i>	Vincke <i>et al.</i> , 2001
<i>Sphingomonas</i>		Vincke <i>et al.</i> , 2001
<i>Stenothrophomonas</i>	<i>maltophilia</i>	Vincke <i>et al.</i> , 2001
<i>Thiobacillus</i>	<i>ferrooxidans</i>	Maeda <i>et al.</i> , 1999 Yamanaka <i>et al.</i> , 2002
<i>Turicibacter</i>	<i>sanguinis</i>	Okabe <i>et al.</i> , 2007
<i>Xylanivorium</i>		Vincke <i>et al.</i> , 2001

The majority of the knowledge on the pathways of hydrogen sulfide oxidation within corroded concrete originates from cultivation studies of microorganisms from concrete surfaces. In most of these studies, elemental sulfur or thiosulfate has been used as source of reduced sulfur for the bacteria (e.g. Milde *et al.*, 1983; Davis *et al.*, 1998; Maeda *et al.*, 1999; Nica *et al.*, 2000). Parker (1945a) tested growth of *Acidithiobacillus thiooxidans* with an atmosphere containing 1% hydrogen sulfide and concluded from this that hydrogen sulfide did not facilitate growth. It was therefore thought, that hydrogen sulfide needed to be chemically oxidized to either thiosulfate or elemental sulfur before microbial production of sulfuric acid could take place. This conception can be found through out the literature (e.g. Islander *et al.*, 1991; Milde *et al.*, 1983). Parker and Prisk (1953) later find that *Acidithiobacillus thiooxidans* does oxidize hydrogen sulfide, however not in as high concentrations as earlier tested.

Based on the investigations of the microorganisms, a number of possible pathways for the oxidation of hydrogen sulfide to sulfuric acid within the heavily corroded concrete have been proposed (Figure 4.1). Parker and Prisk (1953) suggested that oxidation of hydrogen sulfide had elemental sulfur as intermediate. However they also found that the bacteria oxidized thiosulfate with different thionites as intermediates. Islander *et al.* (1991) suggested that the oxidation pathways were pH dependent and that the pathway involving elemental sulfur was dominant at pH lower than 4. Carbonation of the concrete has been found to potentially increase the corrosion rate (Ismail *et al.*, 1993). This effect may be due to the effect of carbon dioxide on the activity of *Acidithiobacillus thiooxidans* (Jaworska and Urbanek, 1997).

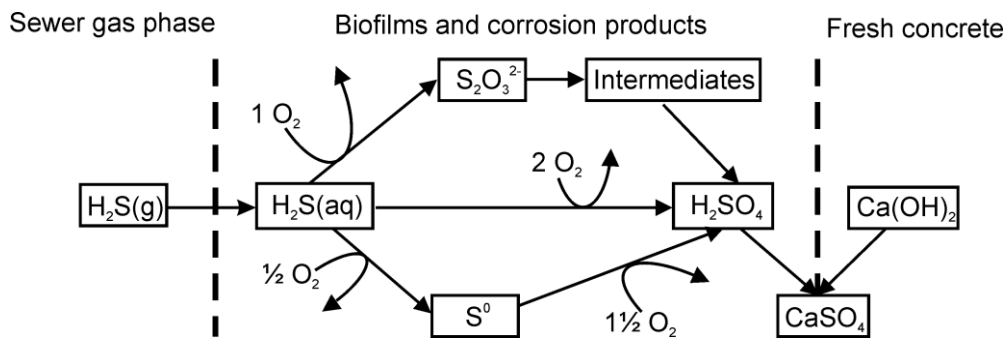


Figure 4.1. Outline of possible reaction pathways for hydrogen sulfide in corroded concrete (Jensen *et al.*, in press (V)).

4.2 Hydrogen sulfide oxidation in corroded concrete – Experimental setup

In this study, the hydrogen sulfide oxidation of the concrete corrosion products was studied by suspending samples of corroded concrete in an acidic solution mimicking the conditions found in the corroded concrete matrix. The suspension was kept in a reactor without headspace and the temperature of the reactor was maintained by placing the reactor in a water bath with temperature control. Mixing was ensured using a magnetic stirrer. In the reactor, the concentration of hydrogen sulfide and oxygen was monitored continuously using an electrochemical hydrogen sulfide sensor (Unisense, Aarhus, Denmark) and a fiber optic oxygen sensor (Presens, Regensburg, Germany) (Figure 4.2) (Jensen *et al.*, subm. (VI); Jensen *et al.*, in press(V)).

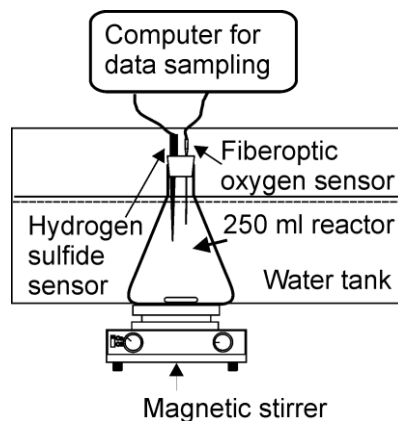


Figure 4.2. Outline of the experimental setup for the study of microbial activity in corroded concrete (Jensen *et al.*, subm. (VI); Jensen *et al.*, in press (V)).

The instrument detection level for the hydrogen sulfide sensor was 0.07 g S m^{-3} determined according to the definition by APHA *et al.* (2005). The sensor measures only H_2S and not the dissociated sulfide forms. As the experiments of this study were all conducted under acidic conditions, the measured H_2S was equal to the total amount of sulfide present in the sample (Jensen *et al.*, in press (V)). The detection limit for the oxygen sensor was stated by the manufacturer to be 20 ppb when measuring DO in liquids (Presens, 2008).

The sampled material was prepared for experiments by suspending sampled corrosion products in deionized water in the Erlenmyer flask shown in Figure 4.2 and 5 mL of nutrient solution was added. The pH of the suspension was adjusted to 1 using 9 M sulfuric acid. The volume of the suspension was adjusted using deionized water until the reactor was completely filled. The pH of 1 was chosen in the experiments because the pH had to be low enough to match the conditions found in the corrosion products, where the pore water pH was as low as or lower than 1 (Section 4.1). The choice of a pH value lower than 1 would have resulted in an increasing uncertainty in the adjustment of the pH as the uncertainty of the pH measurement increases with decreasing pH (Jensen *et al.*, in press (V)).

The gas-tightness of the reactor was tested by filling the reactor with deionized, acidified water in which the oxygen saturation was reduced by purging with nitrogen gas. The oxygen concentration was then monitored in the reactor. Six experiments were carried out. At oxygen concentrations below $2.5 \text{ g O}_2 \text{ m}^{-3}$, the median diffusion of oxygen into the reactor was $8.4 \cdot 10^{-3} \text{ g O}_2 \text{ m}^{-3} \text{ h}^{-1}$ [p₂₅: $5.5 \cdot 10^{-3}$; p₇₅: $1.1 \cdot 10^{-2}$] (i.e. the 25% percentile was $5.5 \cdot 10^{-3} \text{ g O}_2 \text{ m}^{-3} \text{ h}^{-1}$ and the 75% percentile was $1.1 \cdot 10^{-2} \text{ g O}_2 \text{ m}^{-3} \text{ h}^{-1}$) (Jensen *et al.*, in press (V)).

The loss of hydrogen sulfide by adsorption onto the reactor surfaces and by diffusion out of the reactor (e.g. around the rim of the rubber stopper and around the sensors embedded in the stopper) was quantified using deionized water with a pH of 1. A total of 7 determinations were carried out. For these experiments the kinetics of the hydrogen sulfide loss could be described by first order kinetics (Equation 4).

$$\frac{dS_{\text{H}_2\text{S}}}{dt} = -u_{\text{loss}} S_{\text{H}_2\text{S}} \quad (4)$$

Where S_{H_2S} is the hydrogen sulfide concentration [$\text{g H}_2\text{S-S m}^{-3}$] and u_{loss} is the rate constant for auto-oxidation and losses [h^{-1}].

The median rate constant u_{loss} was determined to $7.7 \cdot 10^{-3} \text{ h}^{-1}$ [$p_{25}: 6.1 \cdot 10^{-3}$; $p_{75}: 1.5 \cdot 10^{-2}$] (Jensen *et al.*, in press (V)).

4.3 Hydrogen sulfide oxidation kinetics – Experimental procedure

The kinetics and stoichiometry of hydrogen sulfide oxidation within the corrosion products was investigated by applying the approach described in section 4.2. By simultaneous addition of hydrogen sulfide and oxygen and subsequent measurement of the decline in concentration of both components, the oxidation kinetics and stoichiometry were determined on both sterilized and non-sterilized samples (Jensen *et al.*, in press (V)).

Samples of corrosion products were collected from a sewer manhole near the town of Vårst, situated about 10 km south of Aalborg in the northern part of Denmark. The manhole is located about 1 km downstream of a force main discharge. Samples were collected 3 times in the period from November 13, 2005 to October 30, 2006. The samples were kept refrigerated (4°C) prior to the experiments (Jensen *et al.*, in press (V)). Each experiment was carried out using $14.72 \text{ g} \pm 0.65 \text{ g}$ of sampled corrosion products.

When conducting an experiment, the first step was to determine the consumption of dissolved oxygen for oxidation of accumulated reduced compounds initially present in the sample. Hence it was tested whether oxygen was consumed in the suspension without the addition of hydrogen sulfide. This initial oxygen consumption by the suspended corrosion products was found to be rather high. To reduce interference with the intended experiments, the suspension was therefore kept aerobic for 14 days. During the last 4 days of this period, the oxygen consumption was measured (Time A, Figure 4.3).

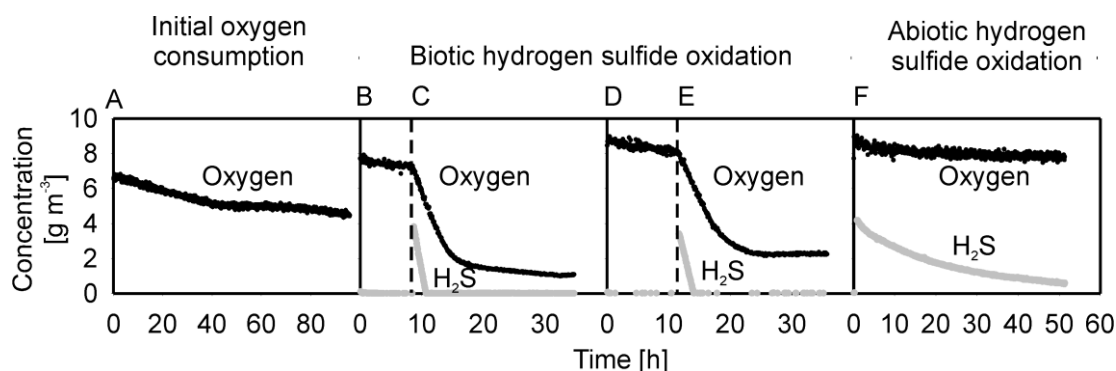


Figure 4.3. Example of measurements. Data is from an experiment with sample from April 19, 2006. Note: Varying time axes. After (Jensen *et al.*, in press (V)).

Following the determination of the background oxygen consumption, the sample was aerated to saturation upon which the reactor was closed (Time B). At the time the oxygen concentration had dropped to about 80% of air saturation, a hydrogen sulfide stock solution was added to a concentration between 2 and $4.5 \text{ g H}_2\text{S-S m}^{-3}$ in the reactor (Time C). This concentration was chosen as it corresponds well to naturally occurring hydrogen sulfide concentrations (Hvitved-Jacobsen, 2002). The hydrogen sulfide stock solution was prepared from washed crystals of disodium sulfide (Na_2S) to a concentration of 1.5 g S L^{-1} . The oxygen measurement was continued

after the depletion of hydrogen sulfide. To obtain a double determination of the oxidation process, the suspension was re-aerated to oxygen saturation (Time D) at the time the oxygen removal rate had stabilized at a level comparable to the background. Hydrogen sulfide was added again when the oxygen concentration had reached about 80% of saturation (Time E).

The kinetics of the abiotic hydrogen sulfide removal was determined in suspension, which was sterilized by autoclaving at 120°C for 20 minutes. Upon cooling to 20°C, the suspension was aerated, hydrogen sulfide added and measurements of dissolved oxygen and hydrogen sulfide were started (Time F) (Jensen *et al.*, in press (V)).

4.3.1 Calculation methods

Previous studies on the abiotic oxidation of hydrogen sulfide in wastewater have reported the oxidation process to follow a power function for both the hydrogen sulfide concentration and the oxygen concentration (Nielsen *et al.*, 2003). A similar relationship is hypothesized valid for the abiotic oxidation of hydrogen sulfide in concrete corrosion products. As the corrosion products are assumed to catalyze the oxidation (Ros *et al.*, 2006), the process is furthermore assumed to depend on the concentration of corrosion products (Equation 5). The concrete corrosion products were quantified by the concentration of total solids.

$$\frac{dS_{H2S}}{dt} = -v_{abio} S_{H2S}^a S_{O2}^b X_{TS} \quad (5)$$

Where v_{abio} is the rate constant for the abiotic hydrogen sulfide oxidation [$\text{g H}_2\text{S-S}^{-0.17}(\text{m}^3)^{1.17} (\text{g TS})^{-1}\text{h}^{-1}$], a is the reaction order for hydrogen sulfide in the abiotic oxidation [-], S_{O2} is the DO concentration [$\text{g O}_2 \text{ m}^{-3}$], b is the reaction order for oxygen in the abiotic oxidation [-] and X_{TS} is the concentration of total solids [g TS m^{-3}].

The experiments performed on sterilized samples include both abiotic oxidation and hydrogen sulfide losses from the reactor due to diffusion and adsorption. The experimental data was therefore simulated as the sum of Equation 5 and Equation 4.

Saturation type kinetics are generally applicable for simulation of bacterial growth processes in suspended cultures, and have been widely applied for simulation of biological processes in sewage systems (Hvitved-Jacobsen, 2002). Applying a yield constant (Y_{SOB}) for growth of bacteria (X_{SOB}) on hydrogen sulfide, the biotic removal of hydrogen sulfide due to bacterial activity is therefore hypothesized to follow Equation 6.

$$\frac{dS_{H2S}}{dt} = \frac{-1}{Y_{SOB}} \mu_{max} \frac{S_{H2S}}{K_{H2S} + S_{H2S}} \frac{S_{O2}}{K_{O2,H2S} + S_{O2}} X_{SOB} \quad (6)$$

Where Y_{SOB} is the yield constant for the sulfur oxidizing biomass in the oxidation of hydrogen sulfide [$\text{g SOB} (\text{g H}_2\text{S-S})^{-1}$], μ_{max} is the specific growth rate of the bacteria [h^{-1}], K_{H2S} is the half saturation constant for hydrogen sulfide [$\text{g H}_2\text{S-S m}^{-3}$], $K_{O2,H2S}$ is the half saturation constant for oxygen in the oxidation of hydrogen sulfide [$\text{g O}_2 \text{ m}^{-3}$] and X_{SOB} is the biomass concentration [g SOB m^{-3}].

The concentration of the hydrogen sulfide oxidizing biomass has not been directly determined in the experiments. However, as the amount of added hydrogen sulfide is small compared to the likely biomass concentration, the biomass concentration is assumed to constitute a constant fraction of the total solids of the corrosion products. As in the case for hydrogen sulfide oxidizing biomass, the yield constant and the maximum specific growth rate could not be determined by the data obtained in the studies conducted. For modeling purposes, these parameters are therefore lumped into one constant (w_{bio}). The biotic oxidation of hydrogen sulfide can consequently be described by Equation 7.

$$\frac{dS_{H_2S}}{dt} = -w_{bio} \frac{S_{H_2S}}{K_{H_2S} + S_{H_2S}} \frac{S_{O_2}}{K_{O_2,H_2S} + S_{O_2}} X_{TS} \quad (7)$$

Where w_{bio} is the rate constant for the biotic oxidation of hydrogen sulfide [$\text{g H}_2\text{S-S (g TS)}^{-1}\text{h}^{-1}$].

Further details on the derivation of Equation 7 are given by Jensen *et al.* (in press (V)).

The experiments performed on non-sterilized samples include biotic oxidation, abiotic oxidation, and hydrogen sulfide losses due to adsorption and diffusion. Like the data for the determination of the abiotic oxidation, the experimental data were simulated as the sum of Equation 5, Equation 7, and Equation 4.

4.4 Biotic and abiotic hydrogen sulfide oxidation kinetics

The abiotic reaction order for hydrogen sulfide, a , (Equation 5) varied from 0.7 to 2.2 with a median value of 1.17. The observed variations in dissolved oxygen concentration were small and did not allow the abiotic oxygen kinetics to be determined. The abiotic oxygen kinetics were consequently assumed to be of zero order, i.e. $b = 0$ (Equation 5). The median value for the parameter v_{abio} was $2.1 \cdot 10^{-7} (\text{g H}_2\text{S-S})^{-0.17} (\text{m}^3)^{1.17} (\text{g TS})^{-1} \text{h}^{-1}$ [p_{25} : $1.2 \cdot 10^{-7}$; p_{75} : $7.2 \cdot 10^{-7}$].

Several studies suggest that the auto-oxidation rate of hydrogen sulfide is strongly pH dependent, as the ionized forms of hydrogen sulfide are oxidized at a higher rate than the un-ionized form. However, only few studies of the auto-oxidation at pH values below 6 exist and these suggest a low auto-oxidation rate (Chen and Morris 1972; Millero *et al.* 1987). The intense heating during the autoclavation of the corrosion product suspension could have altered the surface characteristics of the material. Hence it cannot be excluded that chemically catalyzed hydrogen sulfide oxidation of un-autoclaved corrosion products could differ from the results found.

In the determination of the biotic oxidation kinetics, the oxygen concentration was non-limiting for the biotic reaction. Hence the half saturation constant for oxygen could not be determined and the term in Equation 7 regarding oxygen was omitted. The median value of w_{bio} was $4.1 \cdot 10^{-5} \text{ g H}_2\text{S-S (g TS)}^{-1} \text{h}^{-1}$ [p_{25} : $1.9 \cdot 10^{-5}$; p_{75} : $5.9 \cdot 10^{-5}$]. The median half saturation constant, K_{H_2S} was $1.6 \cdot 10^{-3} \text{ g H}_2\text{S-S m}^{-3}$ [p_{25} : $7.1 \cdot 10^{-4}$; p_{75} : $2.3 \cdot 10^{-3}$]. The rate constant (w_{bio}) was in the same order of magnitude as those reported by Lee *et al.* (2006) and Shinabe *et al.* (1995) when combined with the bacterial counts by Hernandez *et al.* (2002).

From the comparison between the biotic oxidation of hydrogen sulfide and the abiotic oxidation (Figure 4.4), it was found that the median abiotic removal catalyzed by the corrosion products was 1.5% of the biotic hydrogen sulfide oxidation at a hydrogen sulfide concentration of $2.5 \text{ g H}_2\text{S-S m}^{-3}$.

³. Hence, the abiotic hydrogen sulfide removal is in general of minor importance compared to the biotic hydrogen sulfide oxidation. This is in agreement with the findings of Parker (1947).

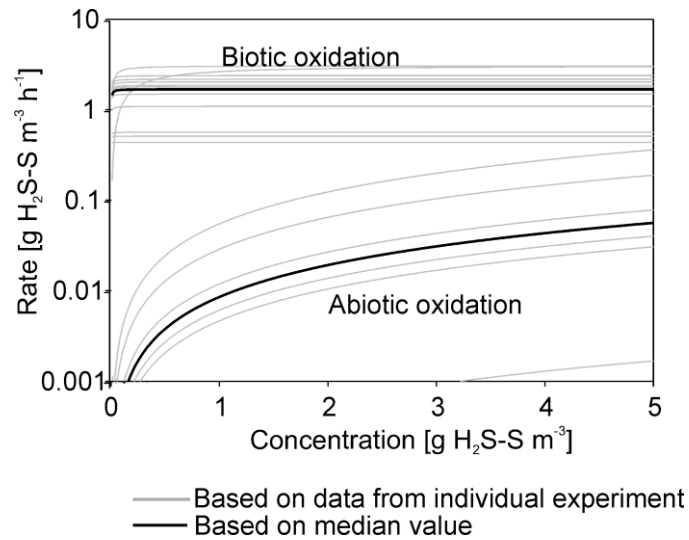


Figure 4.4. Comparison between the simulated rate of the biotic hydrogen sulfide oxidation (Equation 7) and the abiotic oxidation catalyzed by corrosion products (Equation 5) (Jensen *et al.*, in press (V)).

4.5 Stoichiometry of hydrogen sulfide oxidation

The stoichiometric relation between oxygen reduction and hydrogen sulfide oxidation ($\Delta O_2/\Delta H_2S-S$) was determined by comparing corresponding values of oxygen consumption and hydrogen sulfide consumption, as shown in Figure 4.5. The slope of such a graph corresponds to the $\Delta O_2/\Delta H_2S-S$ ratio. The rate of the biotic oxidation was in general much higher than the abiotic removal rate as well as the rate of losses from the reactor. Consequently, when determining the stoichiometry of the biotic hydrogen sulfide oxidation, the influence of abiotic oxidation and loss of hydrogen sulfide from the reactor was neglected.

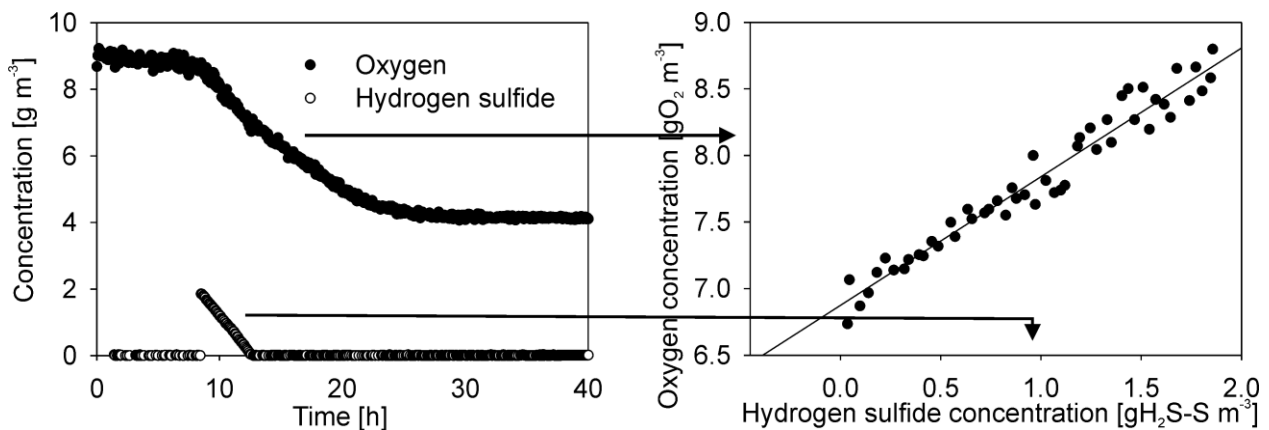


Figure 4.5. Outline of the determination of hydrogen sulfide oxidation stoichiometry by representing the oxygen concentration as function of the hydrogen sulfide concentration. This example is from an experiment on biotic hydrogen sulfide oxidation (Jensen *et al.*, in press (V)).

Calculating the stoichiometry of the abiotic oxidation gave a median $\Delta\text{O}_2/\Delta\text{H}_2\text{S-S}$ ratio of $0.24 \text{ g O}_2 (\text{g S})^{-1}$ [p₂₅: 0.19; p₇₅: 0.44]. The median value is too low to correspond to any of the likely reaction pathways (Figure 4.1). The probable cause is that the abiotic removal rate is of the same order of magnitude as the losses of hydrogen sulfide from the reactor and the diffusion of oxygen into the reactor. I.e. the abiotic oxidation of hydrogen sulfide was too slow to be determined reliably in the setup used.

The stoichiometry of the biotic oxidation of hydrogen sulfide gave a median $\Delta\text{O}_2/\Delta\text{H}_2\text{S-S}$ ratio of $0.61 \text{ g O}_2 (\text{g S})^{-1}$ [p₂₅: 0.52; p₇₅: 0.76]. This ratio indicates an oxygen consumption higher than what is needed for the formation of elemental sulfur, however not high enough to account for the formation of thiosulfate (Figure 4.1). As all hydrogen sulfide was oxidized, it was hypothesized that the main part of the hydrogen sulfide was oxidized to elemental sulfur, while a smaller fraction was oxidized to compounds where sulfur had an oxidation state above zero. The formation of elemental sulfur as an intermediate product in the oxidation of hydrogen sulfide at pH values lower than 4 is in accordance with the findings of Islander *et al.* (1991) and Parker and Prisk (1953). Kleinjan *et al.* (2003) stated that elemental sulfur is stored by the bacteria in globules as long as sulfide is available, hence only oxidized when sulfide is depleted. The formation of elemental sulfur can also explain the yellow color of the corroded concrete surface in Figure 3.3D.

The amount of oxygen consumed from the time of hydrogen sulfide addition until the sharp decline in oxygen removal rate (Figure 4.3) was related to the added amount of hydrogen sulfide to give information on the reactions that took place in the suspension. The median value of these “total” $\Delta\text{O}_2/\Delta\text{H}_2\text{S-S}$ ratios was 1.47. In order to account for a full oxidation of hydrogen sulfide to sulfuric acid, a ratio of 2 would be required (Figure 4.1).

4.6 Hydrogen sulfide oxidation pathway

The left graph in Figure 4.5 shows that oxygen consumption continued at a relatively high rate after hydrogen sulfide had depleted. This was a general tendency in all experiments on biotic hydrogen sulfide oxidation and suggests that an intermediate sulfur compound - formed by the oxidation of hydrogen sulfide - was oxidized after depletion of hydrogen sulfide.

The general pattern of oxygen and hydrogen sulfide consumption was used to further analyze the stoichiometry of the oxidation process. In general, the oxygen consumption in the experiments took place in four stages:

1. prior to addition of hydrogen sulfide, a slow oxygen consumption was observed (as illustrated by the first 8 hours of Figure 4.5)
2. while hydrogen sulfide was present, a rapid oxygen consumption took place (from 8 to 13 hours in Figure 4.5)
3. after hydrogen sulfide had depleted, the rapid oxygen consumption continued (from 13 to 22 hours in Figure 4.5)
4. at some point the oxygen removal rate decreased sharply to a rate lower than in stage 1 (after 27 hours in Figure 4.5)

Based on this analysis, two possible pathways were hypothesized that could describe the observed pattern in hydrogen sulfide and oxygen consumption (Jensen *et al.*, in press (V)). Other possible pathways may also explain the pattern in the oxygen consumption. The pathway illustrated in

Figure 4.6 seems to offer the simplest and most credible explanation for the pattern of the hydrogen sulfide and oxygen consumption. This pathway was therefore chosen for modeling the oxygen data.

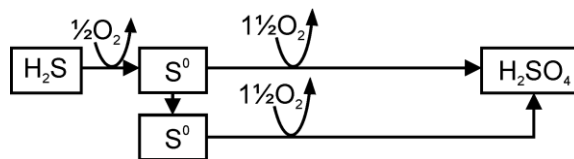


Figure 4.6. The pathway used to describe the hydrogen sulfide and oxygen consumption pattern observed in the experiments on biotic hydrogen sulfide oxidation (Jensen *et al.*, in press (V)).

The hypothesis behind the pathway (Figure 4.6) is that elemental sulfur can exist on two forms, where one form is more readily biodegradable than the other. This could be an intra-cellular form and an extra-cellular form or amorphous and crystalline sulfur allotropes, where it is expected that the amorphous form is more biodegradable than the crystalline form. This theory is in accordance with Kleinjan *et al.* (2005) who proposed the formation of a reactive, “nascent” form of elemental sulfur when the sulfur was produced biologically. The hypothesis is that during stage 1, stored slowly biodegradable elemental sulfur is degraded by the bacteria. When hydrogen sulfide is added in stage 2, the hydrogen sulfide is oxidized to readily biodegradable elemental sulfur, some of which is converted to the less accessible form. While hydrogen sulfide is present in the suspension, hydrogen sulfide is the preferred substrate for the bacteria and only little elemental sulfur is oxidized. After depletion of hydrogen sulfide, the readily biodegradable elemental sulfur is oxidized rapidly (stage 3) and in stage 4, only slowly biodegradable elemental sulfur is present.

The Pathway is furthermore supported by other studies, where a direct conversion of elemental sulfur to sulfuric acid has been reported (Islander *et al.*, 1991; Parker, 1947; Parker and Prisk, 1953; Lizama and Sankey, 1993) and by the study of Parker (1945b) who reports of elemental sulfur being present on corroded concrete surfaces.

A mathematical model of process kinetics and stoichiometry was developed based on the assumed pathway. The processes included in the description of hydrogen sulfide oxidation in suspended concrete corrosion products are:

- *Biotic hydrogen sulfide oxidation*, as described by Equation 7 with readily biodegradable elemental sulfur being the end product.
- *Biotic oxidation of readily biodegradable elemental sulfur*, which is expected to be conducted by the same biomass as the biotic hydrogen sulfide oxidation. The process kinetics are therefore described similarly to the biotic oxidation of hydrogen sulfide. I.e. the oxidation of readily biodegradable elemental sulfur is assumed to follow saturation kinetics with respect to the sulfur concentration and the oxygen concentration.
- *Transformation of readily biodegradable elemental sulfur into slowly biodegradable elemental sulfur*, which is assumed to be proportional to the amount of readily biodegradable elemental sulfur and therefore described by first order kinetics in this component.
- *Biotic oxidation of slowly biodegradable elemental sulfur* is assumed to follow a power function. This is based on the observed patterns in the oxygen consumption before addition of hydrogen sulfide as this oxygen consumption is thought to originate from an oxidation of stored sulfur components. The slowly biodegradable elemental sulfur may be a

heterogeneous mixture of elemental sulfur structures (Steudel, 2000), which might explain why this oxidation can be described by a power function rather than saturation kinetics.

- *Abiotic hydrogen sulfide oxidation*, which is described by Equation 5 with elemental sulfur as the end product. Whether the produced elemental sulfur is readily biodegradable or slowly biodegradable is not known, however, as this oxidation takes place outside the bacterial cells it is assumed to be slowly biodegradable.

These processes are summarized in Table 4.2. The model-matrix gives the equations needed to calculate the changes in concentration of the different components in the model.

Table 4.2. Matrix formulation of the model concept used for simulating the measurements. The rows represent the processes and the columns the involved components.

Component Process	$\frac{\partial S_{H2S}}{\partial t}$	$\frac{\partial S_{sf}}{\partial t}$	$\frac{\partial S_{ss}}{\partial t}$	$\frac{\partial S_{SO4}}{\partial t}$	$\frac{\partial S_{O2}}{\partial t}$	Rate equation
Biotic hydrogen sulfide oxidation	-1	+1			-0.5	$w_{bio} X_{TS} \frac{S_{H2S}}{K_{H2S} + S_{H2S}} \frac{S_{O2}}{K_{O2,H2S} + S_{O2}}$
Oxidation of readily biodegradable elemental sulfur		-1		+1	-1.5	$y_{sf} X_{TS} \frac{S_{sf}}{K_{sf} + S_{sf}} \frac{S_{O2}}{K_{O2,sf} + S_{O2}}$
Conversion of readily biodegradable elemental sulfur to slowly degradable sulfur		-1	+1			$z_s S_{sf}$
Oxidation of slowly degradable elemental sulfur			-1	+1	-1.5	$q_{ss} X_{TS} S_{O2}^c$
Abiotic oxidation of hydrogen sulfide	-1		+1		-0.5	$v_{abio} X_{TS} S_{H2S}^{1.17} S_{O2}^0$

Figure 4.7 shows the measured oxygen concentrations together with the simulations. The parameters used in the simulations are given in Appendix A. Applying the presented hypothesis on the hydrogen sulfide oxidation pathway (Figure 4.6), a good agreement between measurement and simulation was obtained and the measurements did not invalidate the hypothesis. It was therefore believed probable that readily biodegradable elemental sulfur was formed during the oxidation of hydrogen sulfide and subsequently oxidized. Furthermore, the model suggests that the majority of the formed elemental sulfur is oxidized immediately upon depletion of hydrogen sulfide. With the hydrogen sulfide concentration levels used in this study, this corresponds to about 35% of the elemental sulfur formed was converted to slowly degradable elemental sulfur.

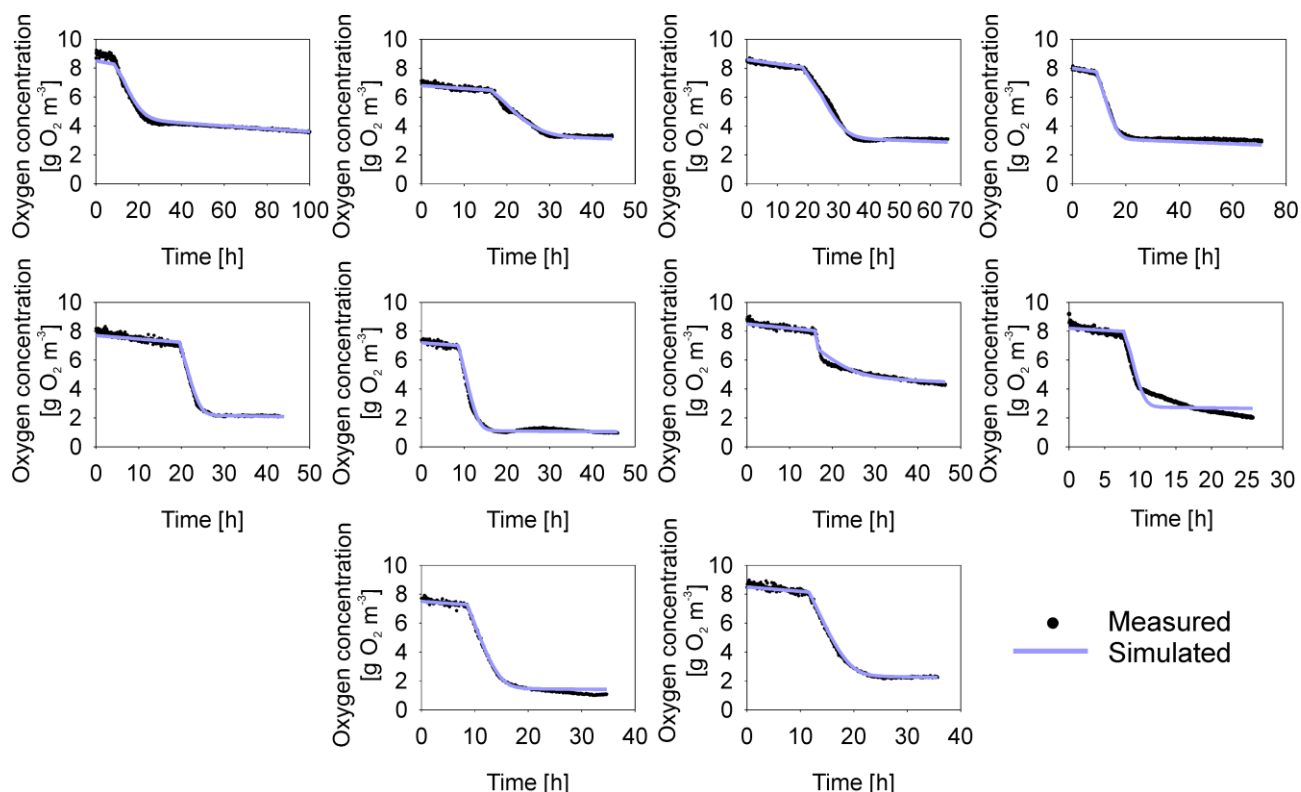


Figure 4.7. Measured and simulated oxygen concentration curves from the experiments on biotic hydrogen sulfide oxidation. In two experiments the data could not be simulated (data not shown) (Jensen *et al.*, in press (V)).

4.7 Determination of surface specific hydrogen sulfide oxidation potential

In order to compare the uptake of hydrogen sulfide from the sewer atmosphere (Section 3) with the oxidation potential measured in suspended samples of corrosion products, samples of corroded concrete were obtained from the pilot scale setup described in section 3.1. The samples were taken from a 20 cm² area of the concrete surface (Figure 4.8). The area for sampling was marked by pressing a metal ring (5 cm in diameter) into the concrete corrosion products. The corrosion products were then sampled with a plastic spoon. During March and April 2008, samples were taken from every second concrete segment in the reactors. No samples were taken from reactor III, which was shut down due to an equipment failure.



Figure 4.8. Photos of a concrete pipe segment after sampling. The sampling area is seen as the light area in the corrosion products (Jensen *et al.*, subm. (VI)).

The samples were then weighed and the hydrogen sulfide oxidation potential was measured in the setup described in section 4.2, to measure the hydrogen sulfide oxidation potential. During the first

30 minutes, measurements were done without the presence of hydrogen sulfide. After 30 minutes, a stock solution of sodium sulfide was added to an initial hydrogen sulfide concentration in the flask of about 3.5 g S m^{-3} . The oxygen concentration started at 90% air saturation and ended at approximately 50% air saturation when hydrogen sulfide had depleted (Jensen *et al.*, subm. (VI)).

The oxidation rates of hydrogen sulfide in the suspended samples of corrosion products were calculated using zero order kinetics. The rates were afterwards related to the sampled concrete surface area where the sample material originated (Equation 8). The results were temperature corrected with an Arrhenius constant corresponding to a non-diffusion limited process (Hvitved-Jacobsen, 2002).

$$r_{susp.} = \frac{r_0 V_{susp.}}{A_{sample}} 1.07^{T-20} \quad (8)$$

Where $r_{susp.}$ is the hydrogen sulfide removal rate in the suspension [$\text{g S m}^{-2} \text{ h}^{-1}$], r_0 is the zero order rate measured in the suspension [$\text{g S m}^{-3} \text{ h}^{-1}$], $V_{susp.}$ is the volume of the suspension [m^3], A_{sample} is the concrete surface area where the tested material was sampled [m^2] and T is the temperature [$^{\circ}\text{C}$].

4.8 Mechanisms for the uptake of hydrogen sulfide on the concrete surface

The surface specific hydrogen sulfide oxidation potentials (Section 4.7) were used to investigate the mechanism of the uptake of hydrogen sulfide in the corroded concrete matrix. These rates were compared to the surface removal rates measurements made in the pilot scale setup. These removal rates were measured and calculated as described in section 3. The measurements used were done in January, March and May 2008.

The visual inspection of the pilot scale reactors in connection with the sampling of corrosion products revealed variations in the thickness of the layer of corrosion products between both the different reactors and between the individual concrete segments of each reactor. Also for a single concrete segment, the layer of corrosion products could vary in thickness, color and texture. Figure 4.8 illustrates the heterogeneity of the corroded surface as color change in the corrosion products around the sample area. The differences are also illustrated by the variations in the mass of the collected samples (Figure 4.9A).

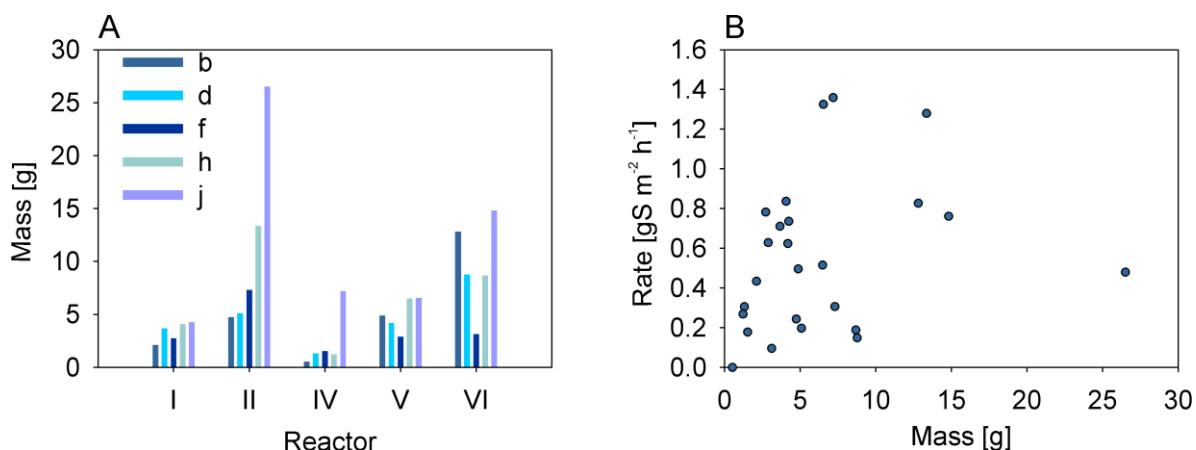


Figure 4.9. A: Mass of the individual samples of corrosion material. B: Zero order rate constant for hydrogen sulfide oxidation as function of the sampled mass (Jensen *et al.*, subm. (VI)).

The correlation between the obtained sample mass and the surface specific hydrogen sulfide oxidation rate was rather weak (Figure 4.9B). Assuming that the concentration of hydrogen sulfide oxidizing biomass was proportional to the hydrogen sulfide oxidation rate, this means that the biomass concentration correlated poorly with the amount of corrosion products which that biomass had caused. One reason for this could be that the bacteria are located in “hotspots” rather than being evenly distributed over the concrete surface. Another possibility is that the bacteria in some segments tended to grow between the gravel still fixed in the concrete matrix and hence were not included in the sampled material. It may also be that some biomass experienced a change in environmental conditions when suspended in the acidic solution, which then could cause a change in biomass activity. As an example, it is possible that pH gradients existed within the corroded concrete and thus that some of the bacteria were therefore adapted to a different pH than the pH of the suspension.

The surface specific hydrogen sulfide oxidation rates measured in suspension and the hydrogen nth order sulfide removal rates in the sewer gas phase (Section 3) were of the same order of magnitude (Figure 4.10). These results were comparable to the uptake rates for hydrogen sulfide in a submerged sewer biofilm reported by Nielsen *et al.* (2005). For oxygen and sulfide concentrations of 6 g O₂ m⁻³ and 2 g S m⁻³, respectively, these biofilms had a sulfide uptake rate of 1.1 g S m⁻² h⁻¹. This is generally just higher than the interval measured in the batch reactor tests, however within the range measured in the sewer gas phase (Figure 4.10). These concentrations were similar to the concentrations used in the batch reactor tests.

Assuming that the potential oxidation rate measured by the batch reactor tests gave a good estimate of the biological activity at the concrete surface, these results indicate that the rate by which hydrogen sulfide was taken up by the concrete surface was governed by a combination of sorption and biological degradation. The hypothesis was that had the removal rate of hydrogen sulfide from the gas phase primarily been governed by biological activity, the removal rate in the gas phase should not have exceeded the potential removal rates measured in the batch reactor tests. On the other hand, had the removal rate in the gas phase primarily been governed by sorption, the potential oxidation rates measured in the batch reactor tests would be expected to be significantly lower than what was observed (Figure 4.10). Based on this it was deduced that both processes were important in the removal of hydrogen sulfide from the sewer atmosphere. Because sorption seems to be important in the removal of hydrogen sulfide from the sewer gas phase, the fate of the hydrogen

sulfide after sorption becomes interesting. If this part of the released hydrogen sulfide does not contribute to the corrosion process, it may lead to overestimation of the corrosion rate. However, if it is available to the bacteria after the hydrogen sulfide supply from the wastewater has stopped, it will contribute to the maintenance of an active bacterial population.

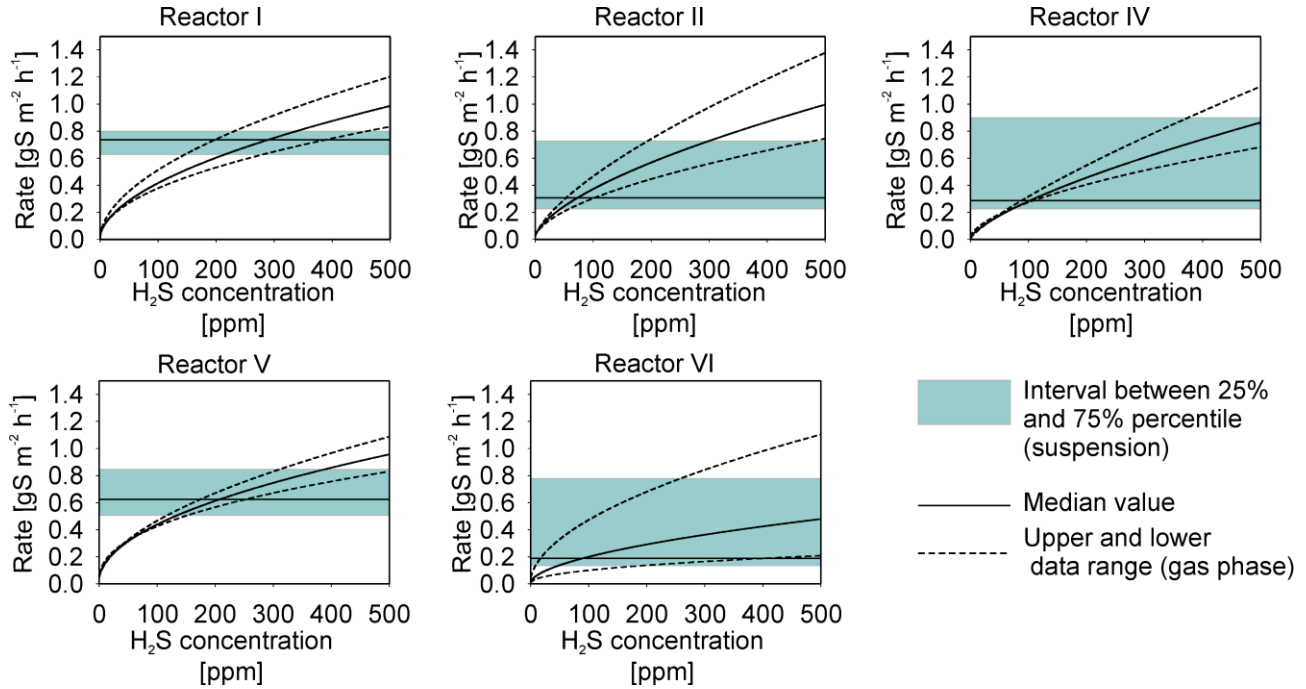


Figure 4.10. Hydrogen sulfide removal rate in the gas phase (n^{th} order) compared to the removal rate of the suspended corrosion products (zero order) (Jensen *et al.*, *subm.* (VI)).

5 Growth of hydrogen sulfide oxidizing bacteria

It has been shown, that the oxidation of hydrogen sulfide is mainly a biological process (Parker, 1947; Jensen *et al.*, in press (V)). In addition, the number of active hydrogen sulfide oxidizing bacteria, within the matrix of corroded concrete, has been identified as a key factor in predicting the corrosion rate of concrete exposed to hydrogen sulfide (Jensen *et al.*, 2008 (VII)). An experimental approach similar to that described in section 4.2 was therefore applied to study the growth kinetics of hydrogen sulfide oxidizing bacteria from corroded concrete when hydrogen sulfide is the source of reduced sulfur.

Like for the determination of the oxidation pathway of hydrogen sulfide in the corroded concrete matrix, the previous studies of the growth kinetics of the important microorganisms has mainly focused on the growth of *Acidithiobacillus thiooxidans* with elemental sulfur as source of reduced sulfur. Table 5.1 shows examples of growth rates determined for *Acidithiobacillus thiooxidans* when the bacteria grow with elemental sulfur as source of reduced sulfur. The growth kinetics of *Acidithiobacillus thiooxidans* with hydrogen sulfide as source of sulfur is not well described in literature. Shinabe *et al.* (1995) reported hydrogen sulfide oxidation kinetics in media inoculated with *Acidithiobacillus thiooxidans*; however, they did not specifically report growth rates.

Table 5.1. Specific growth rates for *Acidithiobacillus thiooxidans* with elemental sulfur as reduced sulfur source.

pH	Specific growth rate d^{-1}	Reference
	2.87	Chen <i>et al.</i> , 2002
0.9-1	0.3	
2.1-2.3	1.5	Rao and Berger, 1971
3.0-3.2	1.2	
4.2-4.3	0.02	
1.5	1.3-3.9	Konishi <i>et al.</i> , 1995
	1.97 ^a	Tichy <i>et al.</i> , 1994
	1.92 ^b	

a) sulfur source: biologically produced elemental sulfur

b) sulfur source: sulfur flower (chemically produced)

5.1 Method for studying the growth of hydrogen sulfide oxidizing bacteria

The growth of the hydrogen sulfide oxidizing bacteria from the corroded concrete was studied using suspensions of the sampled concrete corrosion products similar to what described in section 4.2. To facilitate growth of the bacteria, the setup was automated to ensure the supply of both oxygen and hydrogen sulfide over a longer time period. The details of the setup are described below.

The sample suspension was kept in a reactor in which the oxygen and hydrogen sulfide concentration was measured continuously. The volume of the suspension was adjusted so that the reactor was without headspace. A water bath was used to buffer temperature changes. The reactor was operated in cycles using a PLC control system. In the beginning of each cycle, the reactor was

aerated with atmospheric air for 3 minutes to an oxygen concentration of approximately 80% air saturation. After the aeration, a stock solution of 42 mM sodium sulfide (Na_2S) and 7 M sodium bicarbonate (NaHCO_3) in deionized water was pumped into the reactor. When the oxygen concentration dropped below 50% air saturation, a new cycle started. After growth had been achieved, the addition of sulfide was terminated and the experiment was continued with an addition of a stock solution containing 7 M sodium bicarbonate (Figure 5.1). Sodium bicarbonate was added as source of carbon.

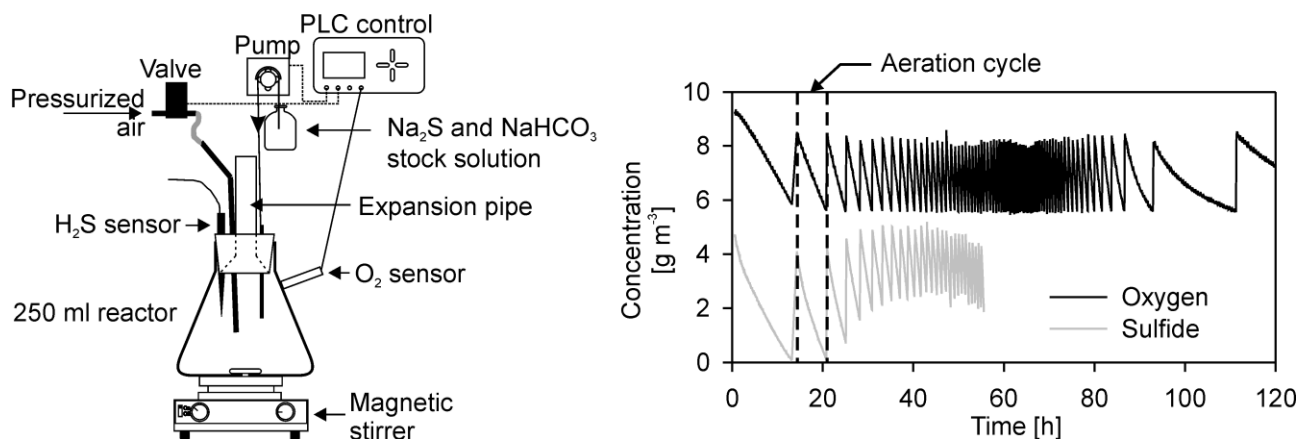


Figure 5.1. Experimental setup and an example of raw data from a growth experiment (Jensen *et al.*, in prep. (VIII)).

The reactor was tested for diffusion of oxygen into the reactor as well as diffusion of hydrogen sulfide out of the reactor and auto-oxidation of hydrogen sulfide within the reactor. The diffusion of oxygen into the reactor was $0.05 \text{ g O}_2 \text{ m}^{-3} \text{ h}^{-1}$ within the oxygen concentration interval of the experiments. The loss of hydrogen sulfide due to diffusion and auto-oxidation was $0.2 \text{ g S m}^{-3} \text{ h}^{-1}$.

5.2 Sample preparation

Two types of experiments were carried out. In the first type, the pH was adjusted using sulfuric acid (H_2SO_4) whereas in the other type of experiments, hydrochloric acid (HCl) was used. The purpose of adjusting pH with hydrochloric acid was to measure the production of sulfate by the bacteria. In order to bring down the initial concentration of sulfate, these samples were subjected to a number of washing steps. The washing consisted of suspension in deionized water, centrifugation, decantation and following resuspension of the sample material. This was repeated up to 9 times.

In the experiments with sulfuric acid for pH adjustment, approximately 15 g of sample material was used for each experiment. In the experiments with hydrochloric acid, approximately 22 g of sample material were used for each experiment, as this procedure also removed part of the bacteria initially present in the sample material.

The washed sample material as well as the unwashed sample material was suspended in deionized water with 5 ml nutrient solution containing $20 \text{ g NH}_4\text{Cl L}^{-1}$, $100 \text{ g KH}_2\text{PO}_4 \text{ L}^{-1}$, $40 \text{ g MgSO}_4 \cdot 2\text{H}_2\text{O L}^{-1}$, $1.5 \text{ g CaCl}_2 \text{ L}^{-1}$, $1 \text{ g FeCl}_3 \cdot 6\text{H}_2\text{O L}^{-1}$, and $1 \text{ g MnSO}_4 \cdot \text{H}_2\text{O L}^{-1}$. The pH of the solution was adjusted to 1. In 5 experiments, this adjustment was done with 9 M sulfuric acid and in another 5 experiments, 6 M hydrochloric acid was used.

5.3 Analytical procedures

Similar to the setup described in section 4.2, the concentration of hydrogen sulfide within the reactor was measured continuously using a hydrogen sulfide sensor (Unisense, Aarhus, Denmark). The oxygen concentration was likewise measured continuously using a fiber optic sensor with a sensor spot (Presens, Regensburg, Germany). pH was measured using pH strips, pH 0-2.5 (Merck, Darmstadt, Germany) 1 to 4 times a day, the frequency increasing with increasing activity within the reactor.

In three of the experiments, where pH was adjusted using sulfuric acid, elemental sulfur was measured using Trace gas chromatograph (Thermo-Scientific, Copenhagen, Denmark) with a Trace mass spectrometer (Thermo-Scientific, Copenhagen, Denmark). Samples were taken 1 to 4 times a day, the frequency increasing with increasing activity in the reactor. Elemental sulfur was extracted by shaking with toluene and the concentration was measured against an internal standard (musk xylene D 15, from Ehrenstorfer, Augsburg, Germany). For three samples, a second extraction was performed to control the extraction efficiency. This revealed efficiencies of 60-70% and with higher uncertainty towards low concentrations. The limit of quantification was found to be approximately 6 g S m^{-3} . The results of the elemental sulfur analysis should therefore be considered as an indication for formation and degradation of elemental sulfur rather as an exact representation of the concentration within the reactor.

In the experiments with washed sample and the pH adjusted by hydrochloric acid, samples for sulfate analysis were taken with the same intensity as the samples for elemental sulfur analysis. The samples were analyzed on ion chromatograph (Dionex DX-600 model 50, Salt Lake City, USA) with an ionpac AS17 column. After washing, the concentration of sulfate in the suspension reached a concentration of approximately $2300 - 3000 \text{ g S m}^{-3}$. This is in the same order of magnitude as the solubility of gypsum under low pH, according to the findings of Aagli *et al.* (2005). As the probable formation of sulfate was much below this level, the results of the sulfate measurements are not presented.

5.4 Calculation procedures

For each experiment, the rate of hydrogen sulfide removal (SUR) and the rate of oxygen removal (OUR) were calculated as the slope of the curves for each aeration cycle (Figure 5.1). The slopes were calculated from the individual data points using the method of least squares. These rates were corrected to a temperature of 25°C according to an Arrhenius-type equation with a temperature coefficient of 1.07 typical for non-diffusion limited processes (Hvitved-Jacobsen, 2002).

The determination of the growth rate was based on the assumption of exponential growth (Equation 9):

$$\frac{dX_{SOB}}{dt} = \mu X_{SOB} \quad (9)$$

Where μ is the growth rate [h^{-1}].

Assuming that an increase in hydrogen sulfide oxidation rate is caused by growth of the hydrogen sulfide oxidizing biomass, equation 10 is derived for the description of the change in hydrogen sulfide oxidation rate:

$$\frac{dS_{H_2S}}{dt} = SUR = \mu \frac{X_{SOB}}{Y_{H_2S}} \quad (10)$$

Where Y_{H_2S} is the yield constant of the biomass with respect to oxygen [g biomass (g S)⁻¹].

A similar equation can be written with respect to the oxygen consumption (equation 11).

$$\frac{dS_{O_2}}{dt} = OUR = \mu \frac{X_{SOB}}{Y_{O_2}} \quad (11)$$

Where Y_{O_2} is the yield constant of the biomass with respect to oxygen [g biomass (g O₂)⁻¹].

These equations were applied to calculate the growth rate from the SUR and OUR curves from each experiment.

The stoichiometry of the oxidation was calculated as the ratio between consumed oxygen and consumed hydrogen sulfide (equation 12).

$$\frac{O_2}{H_2S} = \frac{\int_{t1}^{t2} \frac{dS_O}{dt}}{\int_{t1}^{t2} \frac{dS_{H_2S}}{dt}} \quad (12)$$

The calculations were done using the trapezoidal rule for numerical integration between the individual data points (Kreysig, 1999).

5.5 Development in the hydrogen sulfide and oxygen uptake rates

The rates of hydrogen sulfide removal and oxygen removal showed the same pattern in all experiments (Figure 5.2). Due to equipment failures, graphs I and VIII differ from the rest. The part of the data not affected by the failure is presented. While hydrogen sulfide was present, there was an exponential increase in the uptake rate for both oxygen and hydrogen sulfide. After depletion of hydrogen sulfide, the oxygen removal rate dropped immediately, but only to increase sharply again afterwards and then slowly to decrease. In the following, the part of the experiments where hydrogen sulfide was present is designated stage 1 and the part after depletion of hydrogen sulfide is designated stage 2.

The pattern in oxygen consumption rate can be explained by first oxidation of hydrogen sulfide during stage 1 and afterwards in stage 2 an oxidation of products formed during the hydrogen sulfide oxidation of stage 1.

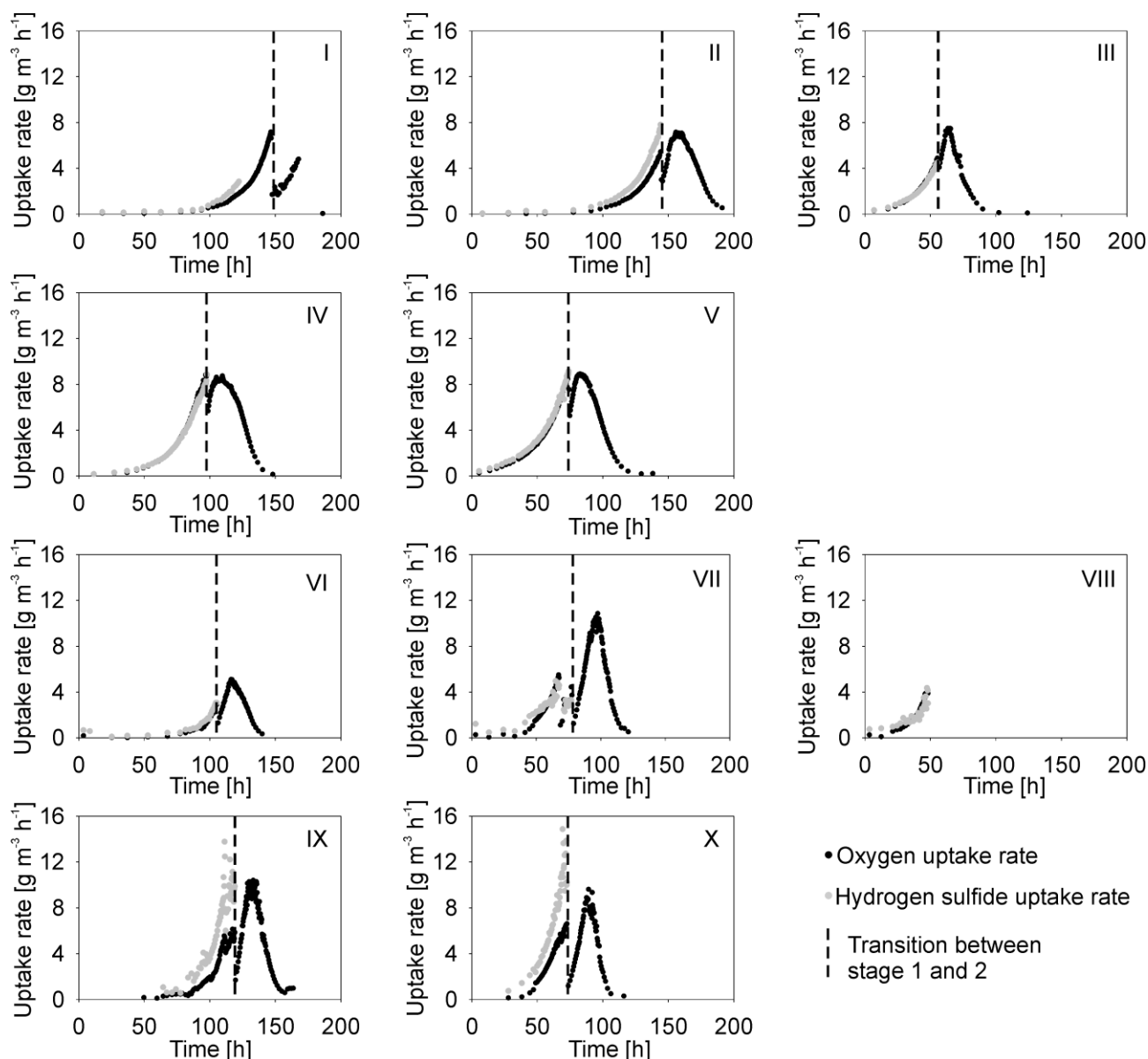


Figure 5.2. Development in uptake rates for hydrogen sulfide and oxygen, respectively. The upper 5 graphs show results from experiments with sulfuric acid and the lower 5 graphs show results from experiments with hydrochloric acid (Jensen *et al.*, in prep. (VIII)).

5.6 Stoichiometry of the growth experiments

For the oxygen removal rate, two areas were calculated for the determination of stoichiometry. The first corresponding to stage 1, the second corresponding to stage 2. Based on these areas, the stoichiometric ratio was calculated according to equation 12. The results are shown in Table 5.2. Using a Student's t-test, it was found that on a 95% level of significance, the difference in the ratios from experiments with sulfuric acid and experiments with hydrochloric acid were not statistically significant. The use of hydrochloric acid for adjustment of pH did not significantly change the stoichiometry of the hydrogen sulfide oxidation. Therefore the median values calculated of the entire dataset are applied in the following.

As described in section 4.1 (Figure 4.1), the oxidation of hydrogen sulfide to elemental sulfur would correspond to a ratio between oxygen and hydrogen sulfide of 0.5, whereas a ration of 1 would correspond to formation of thiosulfate, and a ratio of 2 would correspond to formation of sulfate. The overall ratio between consumed oxygen and consumed hydrogen sulfide for all experiments had a median of 2.24, which is too high to correspond to an overall formation of sulfate. The high ratio can be explained by the first part of the experiments being affected by the loss of hydrogen sulfide from the reactor and the diffusion of oxygen into the reactor. Loss and diffusion occurred during the entire experiment, however, their effect was most important in the initial part of the experiment, where the biological activity was low compared to these effects. For stage 1, the ratio was higher than the ratio corresponding to formation of elemental sulfur, however not high enough to correspond to formation of thiosulfate. This suggests the formation of a mixture of elemental sulfur and sulfur at a higher oxidation state than zero. This is in accordance with the findings of Jensen *et al.*, (in press (V)).

Table 5.2. Stoichiometric coefficients for each part of the experiments as well as the total experiment. The data scatter is quantified as the 25% and 75% percentiles.

	O ₂ /H ₂ S stage 1			O ₂ /H ₂ S stage 2			O ₂ /H ₂ S total		
	median	25% percentile	75% percentile	median	25% percentile	75% percentile	median	25% percentile	75% percentile
H ₂ SO ₄	0.92	0.62	1.00	1.28	1.19	1.59	2.24	1.95	2.60
HCl	0.69	0.51	0.86	1.41	0.86	2.25	2.01	1.36	3.10
Total	0.76	0.62	0.97	1.28	1.05	1.82	2.24	1.62	2.68

The total amount of sulfur added as hydrogen sulfide was compared to the amount of elemental sulfur measured in three experiments (Figure 5.3). These results indicate, that elemental sulfur was formed while hydrogen sulfide was supplied and degraded after hydrogen sulfide had depleted.

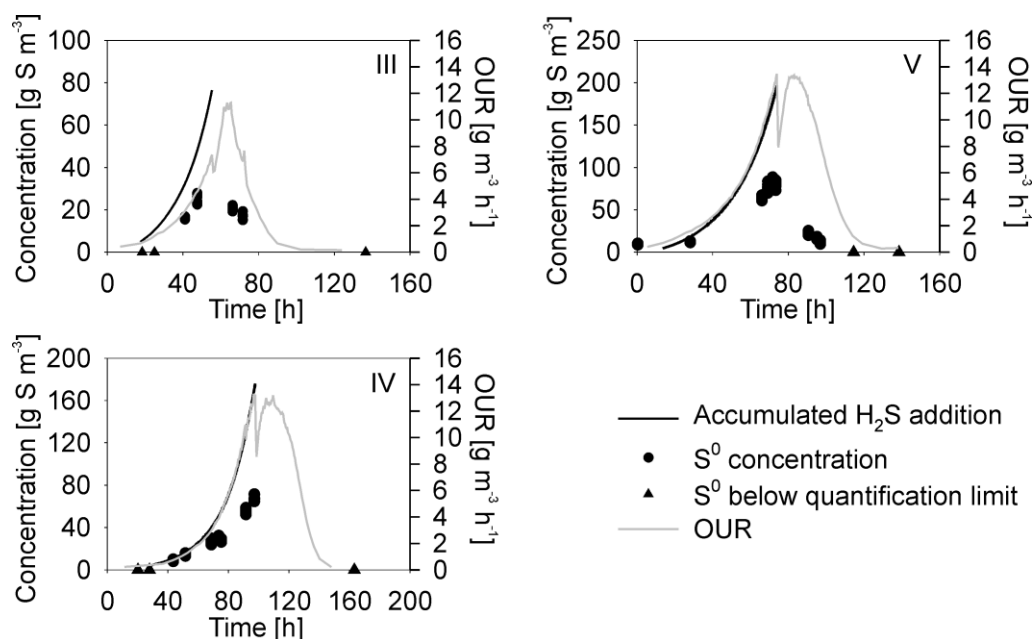


Figure 5.3. Accumulated addition of hydrogen sulfide-sulfur and measured elemental sulfur concentration. The OUR curve illustrates the progress of the experiment. Note: Varying axes (Jensen *et al.*, in prep. (VIII)).

The amount of elemental sulfur extracted from the suspension in the reactor during the experiments increased while hydrogen sulfide was supplied and decreased after hydrogen sulfide depletion (Figure 5.3). Taking into account the analytical recovery rate of elemental sulfur, the elemental sulfur measured, could account for the majority of the sulfur added as hydrogen sulfide. The difference between the added sulfur and the sulfur recovered as elemental sulfur could be explained either as failure to extract this sulfur or as oxidation of the elemental sulfur. The latter was supported by the ratio between oxygen and hydrogen sulfide consumption, which was higher than what was needed for merely formation of elemental sulfur (Table 5.2).

Unlike the findings described in section 4.3 through 4.6 no evidence of the existence of slowly biodegradable elemental sulfur was found in these experiments. There are some studies suggesting, that biologically produced elemental sulfur can change properties over time (Kleinjan *et al.*, 2003). This could mean that the formation of slowly biodegradable elemental sulfur is a result of sub-optimal conditions for the bacteria, where limitation by the lack of other substrates, for example oxygen, prevents the oxidation of stored elemental sulfur. The ageing of the elemental sulfur could then result in the formation of a less biodegradable form.

5.7 Growth rates

The growth rate of the active biomass on hydrogen sulfide was evaluated using the data from stage 1 of each experiment. Hence the increase in oxygen uptake rate and hydrogen sulfide uptake rate were simulated with equation 10 and 11 i.e. the exponential equations describing the growth of hydrogen sulfide oxidizing biomass (Table 5.3). As for the stoichiometric coefficients, it was found that differences between the results from the experiments using hydrochloric acid and the experiments using sulfuric acid for pH adjustment were not statistically significant on a 95% level of significance. Hence the use of hydrochloric acid for pH adjustment did not significantly alter the growth kinetics of the bacteria. It was also tested whether the rates calculated from the hydrogen sulfide uptake rate differed from the rates calculated from the oxygen uptake rate on a 95% level of significance, which was also not the case.

The specific growth rate constant determined for the increase in oxygen uptake rate was higher than the specific growth rate constant determined using the increase in hydrogen sulfide uptake rate. This was the case both for the median values displayed in Table 5.3, but also for each individual experiment, except in two cases. If the assumption is correct that an increase in substrate uptake rate can be caused only by an increase in active biomass, this could be explained in different ways. One possible explanation is that two different microbial species are present in the reactor of which only one oxidizes hydrogen sulfide, however both use oxygen.

Table 5.3. Median values for the growth rates based on the hydrogen sulfide uptake rate and oxygen uptake rate, respectively. The data scatter was quantified as the 25% and 75% percentiles.

	Hydrogen sulfide [d^{-1}]			Oxygen [d^{-1}]		
	median	25% percentile	75% percentile	median	25% percentile	75% percentile
H ₂ SO ₄	1.22	1.12	1.30	1.26	1.19	1.35
HCl	1.32	1.13	1.51	1.77	1.33	1.99
Total	1.25	1.15	1.34	1.33	1.26	1.78

Comparing these growth rates to growth rates reported in the literature (Table 5.1), they are in the same order of magnitude as the specific growth rates reported for growth of *Acidithiobacillus thiooxidans* with elemental sulfur as sulfur source.

In order to predict the lifetime of concrete sewer pipes exposed to hydrogen sulfide, the linkage between the uptake of hydrogen sulfide on the surface and the production of sulfuric acid needs to be determined. This is also crucial for odor and health related prediction of the hydrogen sulfide distribution in sewer networks (Vollertsen *et al.*, 2008 (II)). As the oxidation of hydrogen sulfide and production of sulfuric acid are microbial processes, the prediction of the active biomass present on the surfaces is a key parameter. The growth kinetics of the hydrogen sulfide oxidizing bacteria when supplied with hydrogen sulfide as source of reduced sulfur is therefore interesting. This study shows that under conditions where nutrients, hydrogen sulfide and oxygen are not limiting for the bacteria, the growth rate of the bacteria on hydrogen sulfide is comparable to their growth rate on elemental sulfur. It therefore serves as a first step in predicting the biomass growth on the concrete surfaces based on the release of hydrogen sulfide from the wastewater.

6 Survival of hydrogen sulfide oxidizing bacteria

As described in section 2, the production and subsequent release of hydrogen sulfide to the sewer gas phase is strongly dependent on several chemical and physical parameters. High pH and low temperature will reduce the release of hydrogen sulfide to the sewer atmosphere, but also groundwater infiltration will cause dilution, and consequently lower the concentration of hydrogen sulfide in the wastewater. This causes the release of hydrogen sulfide to fluctuate and the bacteria on the corroding concrete surfaces would experience periods with little – or even without – hydrogen sulfide available as substrate for maintenance and growth. Both low temperature and high ground water infiltration are in Denmark associated with winter conditions.

It was therefore studied, how periods of hydrogen sulfide starvation influences the activity and survival of the hydrogen sulfide oxidizing bacteria in the corrosion products from a heavily corroded sewer concrete surface.

6.1 Determination of the survival of hydrogen sulfide oxidizing bacteria

The activity of the hydrogen sulfide oxidizing bacteria was quantified using the method described in section 4.2, using samples of concrete corrosion products from the sewer manhole in the town of Vårst (further description in section 4.3).

Sample material was collected twice during the study: On the 13th of November 2005 and on the 30th of October 2006. A fraction of each of the two samples was used for characterization of the sampled material with respect to water content, pH and volatile solids content. The two samples were then divided into sub-samples of 12 to 14 g each. The sub-samples were contained in 50 ml centrifugation tubes (polypropylene), which were stored in an underground sewer monitoring station at temperatures similar to *in situ* soil temperatures.

The experimental setup was the same as that described in section 4.2, except that the hydrogen sulfide concentration was measured using the spectrophotometric determination of Cline (1969). Samples for measurement of the hydrogen sulfide concentration were taken with regular intervals, noting the time for each sample. Sampling was continued for 6 hours.

Within the first 6 month from sampling, determination of the hydrogen sulfide utilization rate of a sub-sample was carried out in intervals of about two weeks. Hereafter, hydrogen sulfide utilization rates were determined after 12 and 18 months, respectively. The sub-samples collected in November 2005 were used for experiments during these 18 months whereas the sub-samples collected in October 2006 were used only during the first 4 months after sampling.

A low hydrogen sulfide utilization rate could in principle be caused by a bacterial lag phase, as the duration of one determination was in the range of some hours. It was therefore tested whether a reduced activity was caused by a biological lag phase or by decay of bacteria. For 8 of the sub-samples, the hydrogen sulfide addition was repeated three times on three successive days, resulting in the bacteria being exposed to hydrogen sulfide for a total of up to 18 hours, hereby overcoming the effect of a possible bacterial lag-phase.

The microbial activity was calculated using zero order kinetics, i.e. the slope of the graph was used as measure of the microbial activity. This rate was corrected for auto-oxidation and reactor losses.

6.2 Development in biological activity over time

Over the first half month of hydrogen sulfide starvation, the biological activity remained more or less constant, upon which it steadily declined (Figure 6.1). During the first two months of starvation, the biological hydrogen sulfide utilization rate declined linearly from about 28 $\mu\text{g H}_2\text{S-S g TS}^{-1} \text{ h}^{-1}$ to about 6 $\mu\text{g H}_2\text{S-S g TS}^{-1} \text{ h}^{-1}$; corresponding to a monthly decline in activity of approximately 40%. After two months of hydrogen sulfide starvation, the utilization rate became constant and stayed so until the 12th month. After 18 months of hydrogen sulfide starvation, the utilization rate had dropped to a level not much higher than what could be explained by the rate of auto-oxidation and loss in the test reactor.

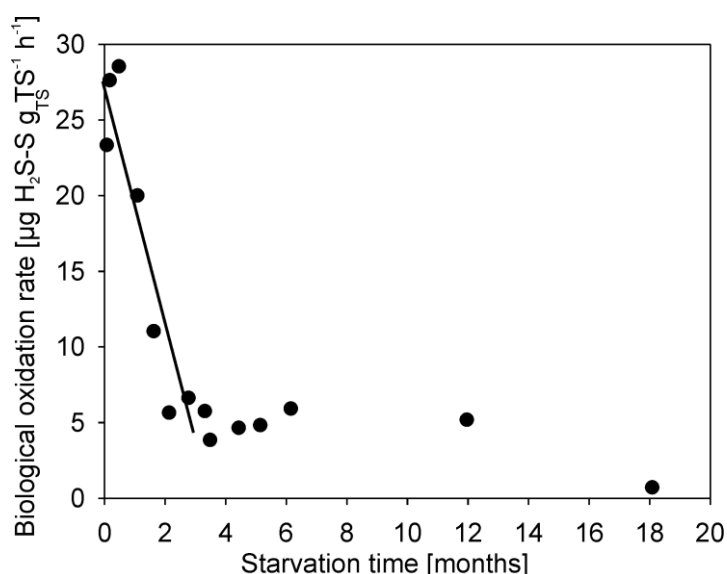


Figure 6.1. Development of the biological hydrogen sulfide utilization rate during hydrogen sulfide starvation. The line indicates the decline in oxidation activity during the first 2.5 months (Jensen *et al.*, 2008 (IX)).

6.3 Regeneration of biological activity

Investigating whether the decline in hydrogen sulfide utilization rate was due to a biological lag phase or whether the involved bacteria had decayed, it became evident that even after 6 months of hydrogen sulfide starvation the major part of the initial activity could be restored within 18 hours of hydrogen sulfide exposure (Figure 6.2).

After 3 to 6 months of starvation and 18 hours of hydrogen sulfide exposure, the activity could be restore to about 80% of the initial activity prior to starvation. After 12 and 18 months of starvation, the activity of the bacteria could not be restored. Indicating that the bacteria survived hydrogen sulfide starvation for at least 6 months, upon which decay of the hydrogen sulfide oxidizing biomass became dominant.

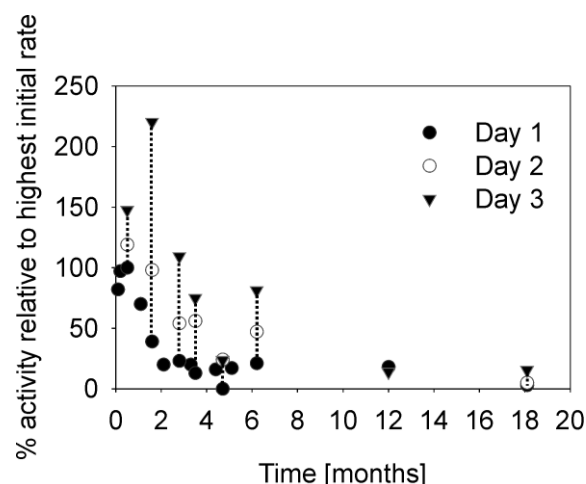


Figure 6.2. The hydrogen sulfide oxidation activity in percent of the maximal initial oxidation rate (Jensen *et al.*, 2008 (IX)).

The experimental evidence indicates that some weeks or months of hydrogen sulfide starvation has little effect on the activity of the hydrogen sulfide oxidizing bacteria. Even if hydrogen sulfide is absent for 6 months at a time, the activity of the hydrogen sulfide oxidizing bacteria appears to be restorable within approximately one day.

A probable explanation for this prolonged survival of the hydrogen sulfide oxidizing biomass is found in the substrate utilization mechanism of the bacteria. Jensen *et al.* (in press (V)) observed that the hydrogen sulfide oxidizing biomass of corroded concrete products form intermediate products when oxidizing hydrogen sulfide. These intermediate products were suggested to mainly consist of elemental sulfur, and seemed to be oxidized at a much lower rate than hydrogen sulfide. This suggests that in hydrogen sulfide rich environments, the intermediate products would tend to accumulate in the corrosion products. This explanation is supported by the findings of e.g. Parker (1945b) and Islander *et al.* (1991) who report a yellowish color of concrete corrosion products, suggesting accumulation of elemental sulfur. This is also visible in Figure 3.3D.

The accumulated intermediate products seem to serve as a reserve-substrate on which the sulfide oxidizing biomass can survive when hydrogen sulfide is absent for longer durations. This feature of long-term survival of the concrete corroding biomass has implications for the operation of sewer systems where hydrogen sulfide occurs at irregular intervals. Such conditions can be found in temperate climates where hydrogen sulfide often is a summer-problem only. Here the bacteria survive the winter and become active in summers when hydrogen sulfide is again present in the sewer atmosphere. Similar conditions exist when hydrogen sulfide control measures are operated inadequately. Where hydrogen sulfide is incompletely controlled, hydrogen sulfide will become available for the bacteria at irregular intervals, however sufficient to allow a continuous corrosion process to proceed – albeit at a lower rate compared to the non-controlled case.

7 Conceptual modeling of hydrogen sulfide in a concrete gravity sewer

The results of the determination of the hydrogen sulfide gas phase removal described in section 3 and the model concept for the hydrogen sulfide oxidation within the concrete corrosion products (Section 4) were combined with the WATS model concept (e.g. Nielsen *et al.*, 2006b; Vollertsen *et al.*, 2005) to simulate corrosion in a concrete gravity sewer (Jensen *et al.*, 2008 (VII)).

7.1 Model scenarios

The simulated scenarios replicate an intercepting gravity sewer line of 1 km downstream of a force main. The hydraulic conditions for the simulations as well as initial sulfide concentrations in the gravity sewer are based on the findings by Nielsen *et al.* (2008 (I)), only the gas phase velocity was increased to 35% of the wastewater velocity based on the findings by (Madsen *et al.*, in prep) (Table 7.1). The additional parameters applied in the simulations are given in Appendix B.

Table 7.1. Physical parameters for the gravity sewer pipe.

Pipe diameter	Slope	Wastewater flow	Wastewater pH	Gas phase velocity
0.5 m	0.3 %	0.01 m s ⁻¹	7.5	35 % of wastewater velocity

The solids in the corroded concrete were regarded as being suspended in the pore water of the matrix. The oxygen concentration in the matrix was assumed to be constant at 0.5 g O₂ m⁻³, based on the oxygen profile measured by Okabe *et al.* (2007) of the outermost part of a heavily corroded concrete sample.

The corrosion process was simulated at bulk water H₂S concentrations considered high (5 g S m⁻³) and at high, low and medium H₂S gas phase removal rates (Table 7.2). After simulating 24 hours of continuous H₂S supply from the sewer bulk water to the sewer gas phase and subsequently to the concrete surface, the H₂S concentration in the bulk water was set to zero and the supply to the gas phase consequently terminated. Hereby the potential corrosion due to the consumption of stored elemental sulfur was evaluated.

Table 7.2. Scenarios for simulation of hydrogen sulfide profiles in the gravity sewer pipe.

Scenario	Wastewater sulfide concentration g S m ⁻³	k_F mg S m ⁻² s ⁻¹ (ppm H ₂ S) ⁻ⁿ	n
low rate	5	0.002	0.5
medium rate		0.006	0.6
high rate		0.010	0.7

The variation in H₂S removal rate is likely to be affected by variations in the concentration of active biomass in the corroded concrete matrix. The biomass concentration in the study by Jensen *et al.* (in press (V)) was evaluated to be relatively low as the samples were taken in a sewer manhole rather than in the sewer pipe it self, where the supply of moisture and nutrients would be higher. This means that the parameter values suggested by Jensen *et al.* (in press (V)) are likely to correspond to the lower range of H₂S gas phase removal rates.

In order to investigate the effect of increased biomass concentration, the measure of biomass in the model was multiplied with 10, 20, 30 and 40, respectively. In these model simulations the high values for gas phase removal rate were applied (Table 7.2). Other studies have reported a broad range of corrosion rates for sewer pipes (e.g. Zhang *et al.*, 2008). Initial model simulations showed that a range in biomass concentration from 1 to 40 times the biomass reported by Jensen *et al.* (in press (V)) would cover the range of reported corrosion rates. In the simulations, H₂S was supplied continuously for 24 hours.

7.2 Predicted corrosion rates

The removal rate of H₂S by the concrete surfaces affects how H₂S is distributed in the sewer atmosphere throughout the gravity sewer pipe. The simulated concentration profile changed with changing gas phase removal rates (Figure 7.1A). At low H₂S removal rates, H₂S was transported further downstream from the force main than for high removal rates. At high removal rates, the H₂S concentrations in the sewer atmosphere became low because more of the H₂S was taken up by the concrete matrix and thereby removed from the sewer atmosphere.

The simulations of the corrosion rate showed that the corrosion of the concrete could be divided into two stages: High corrosion rates due to oxidations of readily biodegradable elemental sulfur and low corrosion rates due to slowly biodegradable elemental sulfur (Figure 7.1B). The corrosion rate due to the oxidation of slowly biodegradable elemental sulfur was of the order of μm per year. In gravity sewers that are full flowing with regular intervals, the corrosion products are washed off, as they are attached only loosely to the concrete surface. This is likely to remove the slowly biodegradable elemental sulfur fraction, which means that this sulfur fraction in practice can be considered as an inert sulfur fraction. The simulations showed that up to 70% of the sulfur supplied to the concrete surface was converted to this inert sulfur. This is in accordance with the findings of Nielsen *et al.* (in prep) and the correction factor suggested by USEPA (1985) for the prediction of corrosion rates.

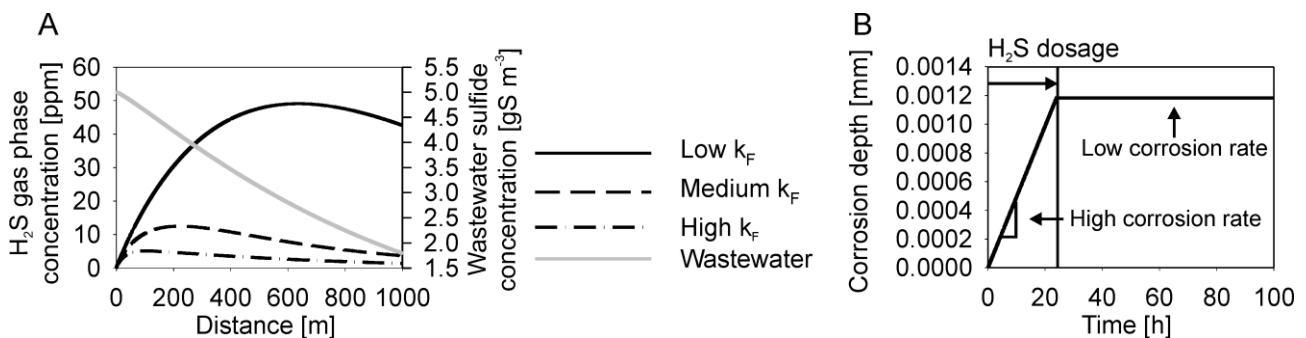


Figure 7.1. A: Concentration profiles for H₂S in the sewer atmosphere and the bulk wastewater through the gravity sewer pipe (cf. Table 7.1 and 7.2). B: Corrosion depth over time exemplified for the high H₂S gas phase removal rate approximately 5 m into the pipe (Jensen *et al.*, 2008 (VII)).

Based on the H₂S concentration profiles shown in Figure 7.1A, the corrosion rates through the gravity sewer pipe were simulated for both low and high gas phase removal rates (Figure 7.2A). These simulations revealed that the corrosion rate was almost independent on the gas phase removal rate. The resulting corrosion rates were about 0.4 mm year^{-1} through the entire simulated sewer pipe

section. As the biomass concentration was evaluated to be low, a scenario replicating a situation with a biomass concentration 20 times higher than that found by Jensen *et al.* (in press (V)) was simulated (Figure 7.2B). This showed corrosion rates changing with the distance from the force main and therefore dependent on the H_2S gas phase concentration. The corrosion rates varied from 2 mm year^{-1} to 7 mm year^{-1} .

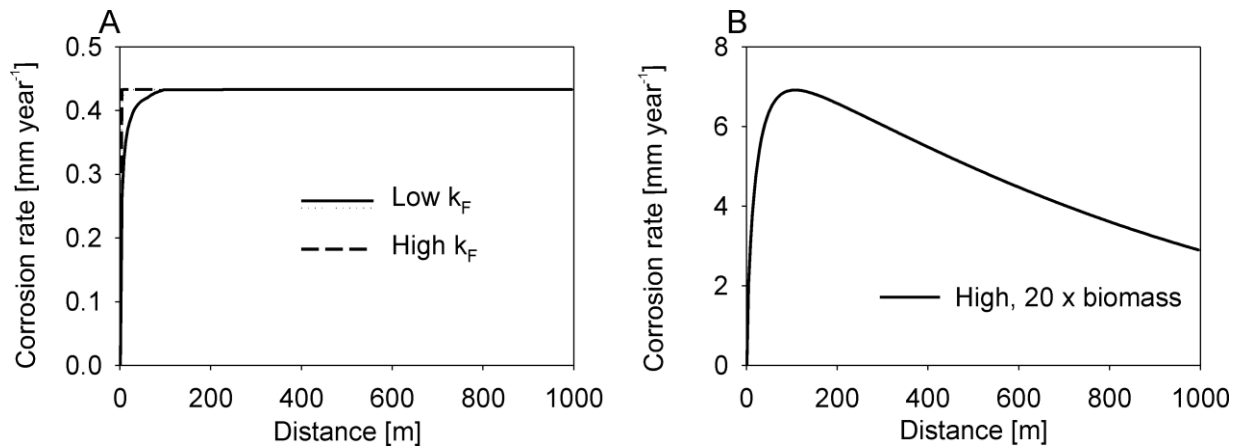


Figure 7.2. Corrosion rates in a gravity sewer downstream of a force main. Corrosion rates at low and high H_2S surface removal rates (A) and a scenario with high removal rates where the active biomass is increased 20 times (B) (Jensen *et al.*, 2008 (VII)).

Comparison between Figure 7.2 and Figure 7.1A illustrates that low gas phase concentration of hydrogen sulfide does not necessarily equal low corrosion rates.

7.3 Corrosion kinetics

The kinetics of the concrete corrosion was calculated using the simulations of the effect of increasing biomass. For each biomass concentration the high corrosion rate (k_F) (cf. Figure 7.1B) at H_2S gas phase concentration varying from 1 to 100 ppm was simulated (Figure 7.3). This showed that the high corrosion rate could be described using saturation type kinetics, and thus does not follow the same type of kinetics as the removal of H_2S from the sewer gas phase (Section 3). It should, however, be noted that this description does not include growth of the bacteria, and this kinetics therefore only is valid for short time periods, where the growth of the hydrogen sulfide oxidizing bacteria is negligible.

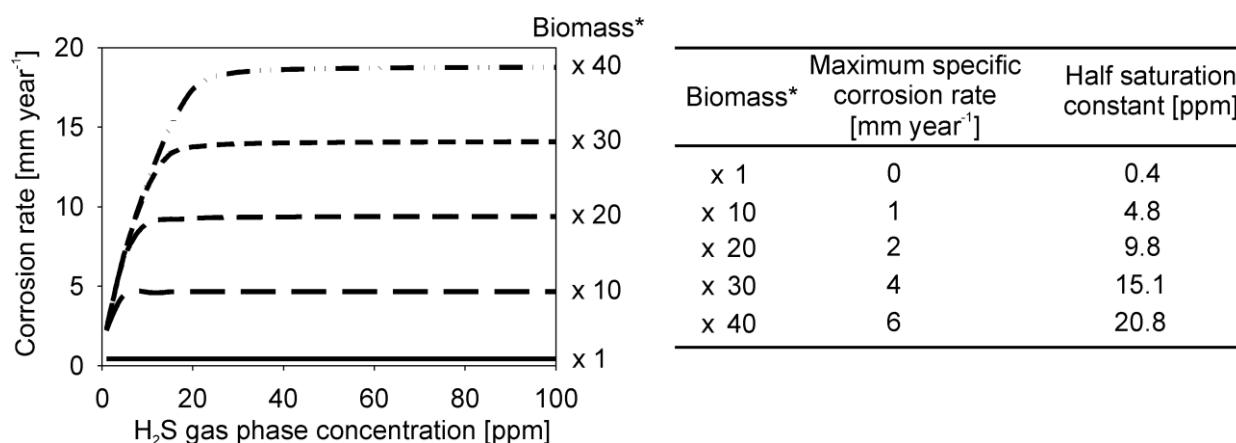


Figure 7.3. Kinetics of the concrete corrosion at varying biomass concentration. *Multiple of biomass concentration found by Jensen *et al.* (in press (V)).

The half saturation constants and maximum specific corrosion rates are shown in Figure 7.3. The values of these parameters were in the same order of magnitude as those reported by *Æsoy et al.* (2002), who found a half saturation constant of 2 ppm and a maximum specific corrosion rate of 16 mm/year. Comparing the maximum specific corrosion rate and half saturation constant found by *Æsoy et al.* (2002) with the values in Figure 7.3 indicates that the biomass in their study was between 20 and 30 times higher than the biomass in the study by Jensen *et al.* (in press (V)).

8 Conclusions

The processes involved in the corrosion of concrete surfaces in sewer networks were studied applying different methods. The uptake of hydrogen sulfide on corroded concrete surfaces was studied in a pilot scale setup, simulating gravity sewer pipes. This study revealed, that uptake of hydrogen sulfide on concrete surfaces is fast compared to release of hydrogen sulfide from the wastewater to the sewer atmosphere. The kinetics of the hydrogen sulfide uptake could be described using n^{th} order kinetics.

The oxidation of hydrogen sulfide within concrete corrosion products was studied in details, focusing on the determination of reaction pathways and description of kinetics. These studies revealed that the oxidation of hydrogen sulfide within the corrosion products was mainly biological. By comparing the potential biological oxidation rate within the corrosion products with the uptake rate of hydrogen sulfide on the concrete surfaces, it was made probable, that sorption kinetics also played a role in the uptake of hydrogen sulfide on the concrete surfaces.

The oxidation of hydrogen sulfide within the corroded concrete products was described using saturation type kinetics and the bacteria could grow exponentially with hydrogen sulfide as source of reduced sulfur.

Elemental sulfur was identified as the key intermediate in the oxidation of hydrogen sulfide to sulfate. Some of the results indicated formation of both readily biodegradable elemental sulfur and slowly biodegradable elemental sulfur. The laboratory experiments carried out to investigate the growth of hydrogen sulfide oxidizing bacteria did, however, not replicate the formation of slowly biodegradable elemental sulfur, which showed that some possible reactions for the elemental sulfur are still unclear.

The results on the uptake of hydrogen sulfide on the corroded concrete surfaces and the kinetics of the hydrogen sulfide oxidation within the corrosion products were combined with the existing WATS model. This combined model concept was then applied to predict the fate of hydrogen sulfide on the concrete surfaces in a simple gravity sewer pipe downstream of a force main. The simulations revealed that the concentration of the hydrogen sulfide oxidizing biomass on the concrete surfaces is a key parameter in the prediction of the corrosion rates as well as for the distribution of hydrogen sulfide in the sewer atmosphere. It was also found, that the slowly biodegradable elemental sulfur could comprise as much as 70% of the sulfur within the corrosion products.

This study has contributed to the knowledge on hydrogen sulfide induced concrete corrosion regarding the process kinetics and stoichiometry. The parameters describing process kinetics and stoichiometry are especially valuable when modeling the fate of hydrogen sulfide within sewer networks, both in terms of predicting corrosion problems and odor nuisances. The results of this study are therefore a further step in the direction of improving the tools for these purposes.

9 Nomenclature and Abbreviations

Abbreviations

DO	Dissolved oxygen
SUR	Sulfide uptake rate
OUR	Oxygen uptake rates

Nomenclature

μ	growth rate [h^{-1}]
μ_{max}	specific growth rate of the sulfide oxidizing bacteria [h^{-1}]
a	the reaction order for hydrogen sulfide in the abiotic oxidation [-]
A_{conc}	concrete surface subject to sewer gas in the pilot scale setup [m^2]
A_{sample}	concrete surface area where the tested material was sampled [m^2]
A_w	the surface area of the wastewater [m^2]
b	the reaction order for oxygen in the abiotic oxidation [-]
c	reaction order for the oxidation of slowly biodegradable elemental sulfur [-]
C_{H_2S}	actual concentration of the wastewater at the specific pH [g S m^{-3}]
$C_{H_2S,Eq}$	dissolved hydrogen sulfide concentration of the wastewater at equilibrium with the gas phase [g S m^{-3}]
F_{H_2S}	surface-specific hydrogen sulfide atmospheric removal rate [$\text{g S m}^{-2} \text{h}^{-1}$]
k_F	surface-specific process rate constant [$\text{g S m}^{-2} \text{h}^{-1} (\text{ppm H}_2\text{S})^{-n}$]
K_{H_2S}	half saturation constant for hydrogen sulfide [$\text{g H}_2\text{S-S m}^{-3}$]
K_{O_2, H_2S}	half saturation constant for oxygen in the oxidation of hydrogen sulfide [$\text{g O}_2 \text{m}^{-3}$]
$K_{O_2, Sf}$	half saturation constant for oxygen in the oxidation of fast biodegradable elemental sulfur [$\text{g O}_2 \text{m}^{-3}$]
K_L	mass transfer coefficient [m h^{-1}]
k_n	gas phase removal rate constant [$\text{ppm}^{1-n} \text{h}^{-1}$]
K_{Sf}	half saturation constant for fast biodegradable elemental sulfur [g S m^{-3}]
M_S	molar mass of sulfur [g mole^{-1}]
n	reaction order of hydrogen sulfide gas phase removal [-]
p_{25}	25% percentile
p_{75}	75% percentile
p_{atm}	atmospheric pressure [Pa]
p_{H_2S}	partial pressure of hydrogen sulfide gas [ppm]
q_{Ss}	rate constant for the oxidation of slowly biodegradable elemental sulfur [$\text{g O}_2 (\text{g TS})^{-1} (\text{g S})^{-1} \text{m}^{-3} \text{h}^{-1}$]
r_0	zero order rate measured in the suspension [$\text{g S m}^{-3} \text{h}^{-1}$]
r_{10}	removal rate of hydrogen sulfide from the sewer atmosphere at 10 ppm hydrogen sulfide [$\text{g S m}^{-2} \text{h}^{-1}$]
r_{100}	removal rate of hydrogen sulfide from the sewer atmosphere at 100 ppm hydrogen sulfide [$\text{g S m}^{-2} \text{h}^{-1}$]
r_{1000}	removal rate of hydrogen sulfide from the sewer atmosphere at 1000 ppm hydrogen sulfide [$\text{g S m}^{-2} \text{h}^{-1}$]
R_{gas}	universal gas constant [$\text{J K}^{-1} \text{mole}^{-1}$]
$r_{susp.}$	hydrogen sulfide removal rate in the suspension [$\text{g S m}^{-2} \text{h}^{-1}$]
S_{H_2S}	dissolved hydrogen sulfide concentration [$\text{g H}_2\text{S-S m}^{-3}$]
S_{O_2}	concentration of DO [$\text{g O}_2 \text{m}^{-3}$]
S_{Sf}	concentration of fast biodegradable elemental sulfur [g S m^{-3}]

S_{Ss}	concentration of slowly biodegradable elemental sulfur [g S m ⁻³]
S_{SO4}	concentration of sulfate [g SO ₄ -S m ⁻³]
T	temperature [°C]
t	time
T_{abs}	absolute temperature [K]
u_{loss}	rate constant for auto-oxidation and losses [h ⁻¹]
v_{abio}	rate constant for the abiotic hydrogen sulfide oxidation [g H ₂ S-S) ^{-0.17} (m ³) ^{1.17} (g TS) ⁻¹ h ⁻¹]
V_{gas}	total gas phase volume in a reactor of the pilot scale setup [m ³]
$V_{susp.}$	volume of the suspension [m ³]
w_{bio}	rate constant for the biotic oxidation of hydrogen sulfide [g H ₂ S-S (g TS) ⁻¹ h ⁻¹]
X_{SOB}	biomass concentration [g SOB m ⁻³]
X_{TS}	concentration of total solids [g TS m ⁻³]
y_{Sf}	rate constant for the oxidation of fast biodegradable elemental sulfur [g S (g TS) ⁻¹ h ⁻¹]
Y_{H2S}	yield constant of the hydrogen sulfide biomass with respect to oxygen [g biomass (g S) ⁻¹]
Y_{O2}	yield constant of the hydrogen sulfide oxidizing biomass with respect to oxygen [g biomass (g O ₂) ⁻¹]
Y_{SOB}	yield constant for the sulfur oxidizing biomass in the oxidation of hydrogen sulfide [g SOB (g H ₂ S-S) ⁻¹]
z_S	rate constant for the formation of slowly biodegradable elemental sulfur [h ⁻¹]

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Appendix A

Parameters used in the hydrogen sulfide oxidation model in section 4.

Parameter	Definition	Unit	Value	
S_{H2S}	Hydrogen sulfide concentration	$\text{g H}_2\text{S-S m}^{-3}$	-	
S_{O2}	Dissolved oxygen concentration	$\text{g O}_2 \text{ m}^{-3}$	-	
S_{sf}	Concentration of fast biodegradable elemental sulfur	g S m^{-3}	-	
S_{ss}	Concentration of slowly biodegradable elemental sulfur	g S m^{-3}	-	
S_{SO4}	Concentration of sulfate	$\text{g SO}_4\text{-S m}^{-3}$	-	
X_{TS}	Total solids concentration	g TS m^{-3}	36944 – 42471	a
X_{SOB}	Concentration of sulfur oxidizing bacteria	g SOB m^{-3}	-	b
u_{loss}	Rate constant for auto-oxidation and losses	h^{-1}	$7.7 \cdot 10^{-3}$	a
v_{abio}	Rate constant for the abiotic hydrogen sulfide oxidation	$\frac{(\text{g H}_2\text{S-S})^{-0.17}}{(\text{m}^3)^{1.17}} (\text{g TS})^{-1} \text{h}^{-1}$	$2.1 \cdot 10^{-7}$	a
μ_{max}	Maximum specific growth rate for the sulfur oxidizing biomass	h^{-1}	-	b
w_{bio}	Rate constant for the biotic oxidation of hydrogen sulfide	$\text{g H}_2\text{S-S (g TS)}^{-1} \text{h}^{-1}$	$1.2 \cdot 10^{-5} - 7.5 \cdot 10^{-5}$	a, f
y_{sf}	Rate constant for the oxidation of fast biodegradable elemental sulfur	$\text{g S (g TS)}^{-1} \text{h}^{-1}$	$1.5 \cdot 10^{-5}$	c
z_s	Rate constant for the formation of slowly biodegradable elemental sulfur	h^{-1}	0.1	c
q_{ss}	Rate constant for the oxidation of slowly biodegradable elemental sulfur	$\text{g O}_2 (\text{g TS})^{-1} (\text{g S})^{-1} \text{m}^{-3} \text{h}^{-1}$	$3.9 \cdot 10^{-8} - 1.1 \cdot 10^{-7}$	d
a	Reaction order for hydrogen sulfide in the abiotic oxidation	-	1.17	a
b	Reaction order for oxygen in the abiotic oxidation of hydrogen sulfide	-	0	b
c	Reaction order for the oxidation of slowly biodegradable elemental sulfur	-	1.3	d
Y_{SOB}	Yield constant for the sulfur oxidizing biomass in the oxidation of hydrogen sulfide	$\text{g SOB (g H}_2\text{S-S)}^{-1}$	-	b
K_{H2S}	Half saturation constant for hydrogen sulfide	$\text{g H}_2\text{S-S m}^{-3}$	$1.35 \cdot 10^{-3}$	a, g
$K_{O2,H2S}$	Half saturation constant for oxygen in the oxidation of hydrogen sulfide	$\text{g O}_2 \text{ m}^{-3}$	0.1	e
K_{sf}	Half saturation constant for fast biodegradable elemental sulfur	g S m^{-3}	0.9	e
$K_{O2,sf}$	Half saturation constant for oxygen in the oxidation of fast biodegradable elemental sulfur	$\text{g O}_2 \text{ m}^{-3}$	0.45	c

^a Determined from the experiments

^b Not determined

^c Determined from modeling of the oxygen data from the experiments

^d Determined from modeling of the background oxygen consumption

^e Determined from sensitivity analysis of the model concept

^f Data normal distributed on 95% level of significance (Lilliefors, 1967)

^g Data not normal distributed on 95% level of significance (Lilliefors, 1967)

For simulation of a measured oxygen concentration, the values of the parameters X_{TS} , q_{ss} , and w_{bio} determined for the experiment in question were applied. For the parameters v_{abio} , c , and a median values were applied and the parameters $K_{O2,H2S}$, y_{sf} , K_{sf} , $K_{O2,sf}$, and z_s were determined by the simulation.

Appendix B

Definition of model parameters used for the simulation of concrete corrosion (Section 7).

Parameter	Definition	Unit	Value
F_{H_2S}	Surface-specific hydrogen sulfide removal rate	$\text{mg S m}^{-2} \text{ s}^{-1}$	-
p_{H_2S}	Partial pressure of hydrogen sulfide	ppm	-
n	Reaction order for gas phase removal	-	0.5 – 0.7
k_F	Surface specific process rate constant	$\text{mg S m}^{-2} \text{ s}^{-1} (\text{ppm H}_2\text{S})^{-n}$	0.002 – 0.010
w_{bio}	Rate constant for the biotic oxidation of hydrogen sulfide	$\text{g H}_2\text{S-S (g TS h)}^{-1}$	$3.94 \cdot 10^{-5}$
X_{TS}	Total solids concentration	g TS m^{-3}	1941176
S_{H_2S}	Hydrogen sulfide concentration in the pore water of the corroded concrete matrix	$\text{gH}_2\text{S-S m}^{-3}$	-
K_{H_2S}	Half saturation constant for hydrogen sulfide	$\text{g H}_2\text{S-S m}^{-3}$	$1.35 \cdot 10^{-3}$
S_{O_2}	Concentration of dissolved oxygen in the pore water of the corroded concrete matrix	$\text{g O}_2 \text{ m}^{-3}$	0.5
K_{O_2, H_2S}	Half saturation constant for oxygen in the oxidation of hydrogen sulfide	$\text{g O}_2 \text{ m}^{-3}$	0.1
y_{sf}	Rate constant for the oxidation of fast biodegradable elemental sulfur	g S (g TS h)^{-1}	$1.5 \cdot 10^{-5}$
S_{sf}	Concentration readily biodegradable elemental sulfur	gS m^{-3}	-
K_{sf}	Half saturation constant for fast biodegradable elemental sulfur	g S m^{-3}	0.9
$K_{O_2, sf}$	Half saturation constant for oxygen in the oxidation of fast biodegradable elemental sulfur	$\text{g O}_2 \text{ m}^{-3}$	0.45
z_s	Rate constant for the ageing of readily biodegradable elemental sulfur	h^{-1}	0.1
q_{ss}	Rate constant for the oxidation of slowly biodegradable elemental sulfur	$\text{gS m}^{-3c} ((\text{gO}_2)^c \text{ gTS h})^{-1}$	$3.5 \cdot 10^{-8}$
c	Reaction order for the oxidation of slowly biodegradable elemental sulfur		1.3

List of papers

- I** Nielsen, A. H., J. Vollertsen, **H. S. Jensen**, H. I. Madsen, T. Hvitved-Jacobsen (2008) Aerobic and anaerobic transformations of sulfide in a sewer system: field study and model simulations. *Water Environment Research* 80(1), 16-25.
- II** Vollertsen, J., A. H. Nielsen, **H. S. Jensen**, T. Wium-Andersen, T. Hvitved-Jacobsen (2008) Corrosion of concrete sewers: the kinetics of hydrogen sulfide oxidation. *Science of the Total Environment*, 394(1), 162-170.
- III** Nielsen, A. H., J. Vollertsen, **H. S. Jensen**, T. Wium-Andersen, T. Hvitved-Jacobsen (2008) Influence of pipe material and surfaces on sulfide related odor and corrosion in sewers. *Water Research*, 42(15), 4206-4214.
- IV** Vollertsen, J., A. H. Nielsen, **H. S. Jensen**, T. Hvitved-Jacobsen (2008) Modeling the Formation and Fate of Odorous Substances in Collection Systems. *Water Environment Research* 80(2), 118-126.
- V** **Jensen, H. S.**, A. H. Nielsen, T. Hvitved-Jacobsen, J. Vollertsen (in Press) Modeling of hydrogen sulfide oxidation in concrete corrosion products from sewer pipes. In press for *Water Environment Research*.
- VI** **Jensen, H. S.**, A. H. Nielsen, P. Lens, T. Hvitved-Jacobsen, J. Vollertsen. Hydrogen sulfide removal by corroding concrete – a comparison between surface removal rates and biomass activity. *Submitted to Environmental Technology*.
- VII** **Jensen, H. S.**, A. H. Nielsen, T. Hvitved-Jacobsen, J. Vollertsen (2008) Hydrogen sulfide initiated corrosion in concrete sewers – a conceptual approach for prediction. Proceedings from the 11th International Conference of Urban Drainage 31. August – 5. September 2008.
- VIII** **Jensen, H. S.**, P. Lens, J. L. Nielsen, K. Bester, A. H. Nielsen, T. Hvitved-Jacobsen, J. Vollertsen (in preparation) Growth of hydrogen sulfide oxidizing bacteria from corroded concrete
- IX** **Jensen, H. S.**, A. H. Nielsen, T. Hvitved-Jacobsen, J. Vollertsen (2008) Survival of hydrogen sulfide oxidizing bacteria on corroded concrete surfaces of sewer systems. *Water Science and Technology* 57(11), 1721-1726.