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## **Ferrous and Ferric Iron Treatment of Sewer Force Main Biofilms**

*The Influence of Sulfide Abatement*

Kiilerich, Bruno

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# **FERROUS AND FERRIC IRON TREATMENT OF SEWER FORCE MAIN BIOFILMS**

THE INFLUENCE OF SULFIDE ABATEMENT

**BY  
BRUNO KIILERICH**

DISSERTATION SUBMITTED 2018



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by

Bruno Kiilerich

Dissertation submitted in 2018

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## ENGLISH ABSTRACT

Transport of wastewater in sewer systems inevitable results in development of sulfides when anaerobic conditions arise in biofilms growing on the sewer pipes. The presence of sulfides in wastewater is a well-recognized problem worldwide, as it gives rise to malodors in the urban atmosphere, corrosion of sewer assets, and possible health issues for service personnel. Consequences which all have profound economic impacts for water utilities. Precipitation of sulfides with ferrous and ferric iron is routinely applied for abatement, with addition taking place at the start of the force main. However, how the presence of iron salts and the precipitated ferrous sulfide influence force main biofilms is largely unknown. In applications where start-of-pipe abatement is infeasible, an end-of-pipe dosing strategy must be adapted. Consequently, the precipitation kinetics of sulfides, which of today is unknown, must be known to ensure proper conversion before discharge of wastewater from the force main.

The influence on biofilm in biochemical, microbiological and physical manners, due to ferrous and ferric iron treatment, were studied using a combination of *in situ* and laboratory experiments. Experiments were conducted using mature biofilms from a pilot scale force main conveying fresh municipal wastewater. Wastewater in the force mains were treated with either ferrous or ferric iron for abatement of sulfide, hence ferrous sulfide would form during retention in the mains. Precipitation kinetics of sulfides were investigated in laboratory setups using different wastewaters. Experiments were conducted under pH conditions typical for municipal wastewater, and at iron to sulfide ratios close to stoichiometric requirements.

It was shown that the addition of iron salts, besides precipitation of sulfides, influenced biofilm activities, microbiomes and diffusivities. Alongside the reduction of activity and separation of microbiomes, experienced for both iron salts, ferric iron exhibited severe effects on diffusivity in the biofilm. It was furthermore shown, that the rate of sulfide precipitation using ferrous and ferric iron must be considered during end-of-pipe abatement. Ferric iron exhibited the fastest and most efficient precipitation under the conditions tested. The precipitation rate was found to be independent of wastewater constituents for ferrous iron, whereas ferric iron was influenced to some extent. Model equations for estimation of kinetic rate constants were proposed, and it was found that precipitation using ferrous iron was governed by pH as well as the iron to sulfide ratio, while ferric iron precipitation solely was controlled by pH.

This study has contributed to knowledge that can be used to improve conceptual sewer models in estimation of sulfide production in iron treated force mains. The findings of the present study can furthermore find practical application in decision making for positioning chemical injection points when using end-of-pipe abatement strategies.





## DANSK RESUME

Transport af spildevand i afløbssystemer resulterer uundgåeligt i dannelse af sulfid, når der opstår iltfrie forhold i biofilmen, der gror på spildevandsrørene. Dannelse af sulfid i spildevand er et globalt anerkendt problem, da det giver anledning til lugtgener i det urbane miljø, korrosion af kloaksystemets komponenter og mulige sundhedsmæssige problemer for driftspersonalet. Problemer som allesammen har store økonomiske konsekvenser for driftsselskaberne. Udfældning af sulfid med ferro- og ferrijern bruges rutinemæssigt til bekæmpelse, hvor jerntilsætningen foretages i begyndelsen af trykledningen. Hvordan jernsalte og den udfældede jernsulfid påvirker biofilmen i trykledningerne er stort set ubeskrevet. I systemer hvor tilsætning af jernkemi i begyndelse af trykledningen, giver utilstrækkelig bekæmpelse, må en strategi, hvor kemi tilsættes i slutningen af trykledningen benyttes i stedet for. Dette betyder, at reaktionshastigheden af jernsulfid udfældning, må kendes, for at sikre tilfredsstillende bekæmpelse, før spildevandet forlader trykledningen.

Den biokemiske, mikrobiologiske og fysiske påvirkning af biofilm, behandlet med ferro- og ferrijern, blev undersøgt i en kombination af *in situ* og laboratorieforsøg. Undersøgelserne blev udført med fuldt udviklet biofilm fra pilot skala trykledninger, der transporterede frisk kommunalt spildevand. Spildevandet var behandlet med enten ferro- eller ferrijern for bekæmpelse af sulfid, og jernsulfider udfældede derfor i trykledningerne. Udfældningskinetikken af sulfid, blev undersøgt i laboratoriet med forskellige typer af spildevand. Forsøgene blev udført ved pH forhold typisk for kommunalt spildevand, og jern-til-sulfid ratioer omkring det støkiometriske behov.

Det blev vist, at tilsætning af jernsalte, ud over udfældning af sulfid, influerede på aktiviteten, mikrobiomet og diffusiviteten af biofilmen. Foruden reduktion af aktiviteten og en separation af mikrobiomet, observeret for begge jernsalte, nedsatte ferrijern diffusiviteten af biofilmen mest udtalt. Derudover blev det vist, at udfældningshastigheden af sulfid med ferro- og ferrijern bør tages i betragtning, når sulfid bekæmpes i spildevandet lige før udløb af trykledningen. Ferrijern udviste den hurtigste og mest effektive udfældning under de undersøgte forhold. Spildevandstypen influerede ikke på udfældningshastigheden for ferrojern, hvorimod typen i nogen grad influerede hastigheden ved brug af ferrijern. Modellinger til bestemmelse af den kinetiske hastighedskonstant blev fremsat. Det blev fundet, at udfældning under anvendelse af ferrojern blev styret af såvel pH som jern-til-sulfid ratioen, medens sulfid udfældning med ferrijern udelukkende blev styret af pH.

Resultater fra dette studie har bidraget til viden, der kan bruges til at forbedre konceptuelle spildevandsmodeller i forudsigelsen af sulfidproduktion i trykledninger behandlet med jernsalte. Resultaterne fra studiet kan endvidere finde praktisk anvendelse i beslutningsprocessen for positionering af kemikaliedosering, når der skal udføres bekæmpelse af sulfid i spildevand før udløb fra en trykledning.



# PREFACE

This thesis has been submitted for assessment in partial fulfilment of the PhD degree. The thesis is based on the scientific papers listed after this preface. As part of the assessment, co-author statements have been made available to the assessment committee and are also available at the Faculty.

This industrial PhD study was carried out in a cooperation between Grundfos Holding A/S and Aalborg University, Department of Civil Engineering, under the Division of Water and Environment in the period from January 2015 till April 2018.

Certain parts of the PhD study were co-supervised by Statens Serum Institut and included a cooperation with Novo Nordisk Foundation Center for Basic Metabolic Research at Copenhagen University. A research cooperation with Karlsruhe Institute of Technology, Chair of Water Chemistry and Water Technology was furthermore established.

The thesis is based on one published paper and the four scientific manuscripts. Contents of the papers are briefly discussed in the extended summary of the thesis. Additional details are given in the paper and manuscripts.

At this point I would like to address a thank you to my supervisors for guidance and support throughout the work with this thesis. A special thanks to Jes Vollertsen who always found time for discussing things, even though his time was not there, and for encouraging me in tough times with his positive and optimistic attitude.

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## LIST OF PAPERS

- I. **Kiilerich, B.**; van de Ven, W.; Nielsen, A. H.; Vollertsen, J. Sulfide precipitation in wastewater at short timescales. *Water* **2017**, *9*, 670, doi:10.3390/w9090670
- II. **Kiilerich, B.**; Nielsen, A. H.; Vollertsen, J. (**2018a**) Kinetics of sulfide precipitation with ferrous and ferric iron in wastewater (Submitted to *Journal of Environmental Engineering*)
- III. **Kiilerich, B.**; Kiilerich, P.; Nielsen, A. H.; Vollertsen, J. (**2018b**) Variations in activities of sewer biofilms due to ferrous and ferric iron dosing (Submitted to *Water Science and Technology*)
- IV. **Kiilerich, B.**; Brejnrod, A. D.; Vollertsen, J.; Kiilerich, P. (**2018c**) Variations in microbiome composition of sewer biofilms due to ferrous and ferric iron dosing (Title is tentative) (not submitted)
- V. **Kiilerich, B.**; Wagner, M.; Nielsen, A. H.; Vollertsen, J. (**2018d**) Apparent diffusion coefficients in sewer force main biofilms treated with iron salts (Title is tentative) (not submitted)



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# 1. INTRODUCTION

In an engineering context of problem solving according to Sharp (1991) there is no “correct solution”, there are several alternatives that must be evaluated to find the “best” suited solution for the specific problem in question. An example of such, is the sewer system, which, from a hydraulic and health perspective, has been the “best” suited solution to urban drainage evolved over many years of engineering. Sewer systems in a primitive form date back to the Minoan and Indus Valley civilization around 2500 BC. The Greek civilization around 300 BC to 500 AD also had sanitation and were forerunners for modern systems, where drains from houses were connected to closed conveyance system guiding the wastewater away. The Romans partly recognized the potential health issues with not having collection systems and they constructed complex branched networks. Additionally, these systems were typically also a means of protection against flooding of the urban areas. From the time of collapse of the Roman empire and until the 17<sup>th</sup> century, sewer systems were more or less overlooked and knowledge on construction and management got lost. In the 17<sup>th</sup>-18<sup>th</sup> hundreds, sewer systems were again being constructed in countries such as England, Germany, France and Italy in an effort to remove the foul smell from the streets and epidemic outbreaks. Since that time, wastewater collection systems have been refined to what we know today (de Feo et al., 2014; Hvitved-Jacobsen et al., 2013; Lofrano and Brown, 2010). This refinement has been in relation to the conveyance capacity of the wastewater, thus the hydraulics of the systems, largely neglecting the biological processes taking place (Hvitved-Jacobsen et al., 2013). The hygienic aspects of sewer systems are today widely recognized together with their hindrance of environmental pollution, if the flow stream is guided to a wastewater treatment plant for purification (Hvitved-Jacobsen et al., 2013; Metcalf and Eddy, 2003). Sewer networks are hence extremely important, but for many an invisible component of the urban infrastructure. For modern urbanization it is in fact one of the most critical assets, as malfunctioning can cause pathogenic exposure, unhygienic conditions, pollution of receiving waters, road damages etc. (Hahn et al., 2002). These underground systems consist of sections where wastewater runs by gravitation in partly filled mains, and of sections where the wastewater must be forced further by pumping action. The force main pipelines are flowing full of wastewater and are used to e.g. lift wastewater over a hill or for conveyance in flat areas where gravitational systems cannot be constructed.

## 1.1. GENERATION AND RELEASE OF SULFIDE

With the conveyance of wastewater in sewer systems, other problems follow, one of them being the formation of sulfides. During conveyance of wastewater from the sources in the catchment area to the wastewater treatment plant, a degradation of its organic and inorganic constituents takes place. This degradation is due to the biological activity primarily taking place in the sewer sediments and biofilms

colonizing the submerged parts of the system (ASCE, 1989; Boon, 1995). When available in the wastewater, oxygen, nitrate, and ferric iron is used as electron acceptors for the degradation. However, when these electron acceptors are depleted, anaerobic conditions prevail. Under anaerobic conditions the sulfate reducing bacteria thrive. These bacteria perform dissimilatory sulfate reduction where they utilize sulfate as electron acceptor for oxidation of organic matter. During this process sulfide is generated and most of it is released to the bulk wastewater flow (Boon, 1995; Hvitved-Jacobsen et al., 2013). The generation of sulfide is influenced by different factors in the wastewater such as the available organic matter and temperature. Furthermore, the sewer system layout and operational pattern also influences the generation of sulfides, where systems with long anaerobic retention times will increase the generation (Boon, 1995; Hvitved-Jacobsen et al., 2013; Park et al., 2014).

Whether sulfide will become a problem depends very much on wastewater pH, as it is only the gaseous sulfide emitted from the wastewater that cause problems in sewer systems. Being a weak diprotic acid, sulfide can be present on different forms. At pH conditions between 6 and 8, which is typical for municipal wastewater, sulfide will be present as hydrogen sulfide ( $\text{H}_2\text{S}$ ) and the bisulfide ion ( $\text{HS}^-$ ). The dissociation constant of sulfide is 7.0 (at 20 °C) which means that 50% will be on the molecular  $\text{H}_2\text{S}$  form and the rest will be on the ionic  $\text{HS}^-$  form. Decreasing pH will shift the equilibrium towards the molecular form, which can be emitted from the wastewater (Yongsiri et al., 2000). Release of  $\text{H}_2\text{S}$  from the wastewater can take place where there is a free water surface and is, beside pH, influenced by temperature and turbulence (Yongsiri, 2004). Locations with high turbulence are hotspots for sulfide release. These are normally found at manholes and pump station wet wells where wastewater is discharged from a force main, or at sewer drop structures (Apgar and Witherspoon, 2007; Matias et al., 2017b). At these locations sulfide can build up in the sewer atmosphere and cause problems.

Sulfide generation is not a problem restricted to warmer climates, it is present worldwide where force mains are found and can thus be generated and cause problems from the cold norths to the sunny souths in countries such as Spain (Rodríguez-Gómez et al., 2005), Portugal (Matias et al., 2017a), Austria (Bertrán de Lis et al., 2007), Germany (Barjenbruch, 2003; Kaempfer and Berndt, 1999), Sweden (Bäckström et al., 2010), Denmark (Nielsen et al., 2008b), Russia (Vasil'ev et al., 2013), USA (Oviedo et al., 2012; USEPA, 1991a; Vollertsen et al., 2015), Canada (Hewayde et al., 2007), Australia (Ganigue et al., 2011; Gold Coast Water, 2007), New Zealand (Christchurch City Council, 2017), Hong Kong (Hong Kong Drainage Services Department, 2016), and United Arab Emirates (Vollertsen et al., 2011).

## 1.2. CONSEQUENCES OF SULFIDE RELEASE

Three main problems are associated with sulfide release from wastewater. These problems are odor nuisance in the urban atmosphere, health issues for sewage workers and corrosion of sewer assets.

When gaseous sulfide escapes the sewer system because of ventilation, it gives rise to odor nuisances in the vicinity. Sulfide has an extremely low odor threshold and the easily recognizable smell of rotten eggs can be detected at a concentration as low as 2 ppb (Apgar and Witherspoon, 2007). Odors from sewer systems are taken seriously by most water utilities. In the city of Toronto they actively seek out areas prone to odor in dedicated studies to react proactively (Hewayde, 2005). In San Francisco it is a priority for the Wastewater Enterprise to keep odor nuisances to a minimum (Vollertsen et al., 2015), and a 24-hour odor complaint hotline has been established so the sewer operation crew can respond to the call and investigate the problem (San Francisco Public Utilities Commission, 2009). In certain areas in Australia water authorities may even receive fines for odor nuisances originating from the sewer system (Gold Coast Water, 2007).

In addition to its offensive smell, sulfide is also a potential health risk to maintenance personnel. Exposure to sulfide gas can at concentrations around 10 ppm cause nausea, give headache, and throat and eye irritation. When concentrations increase it can also cause damage to various parts of the body such as eyes, lungs, olfactory parts, nervous system, heart, blood, brain, gastrointestinal system, and liver (Beauchamp et al., 1984; C.-H. Selene J. Chou, 2003; Fuller and Suruda, 2000; Snyder et al., 1995).

Sulfide is extremely toxic and may be lethal. This happens when a high concentration of sulfide exceeds the detoxification capacity of the body which inhibits aerobic metabolism (C.-H. Selene J. Chou, 2003; Knight and Presnell, 2005). Sewer gas (including mine gas and methane) has been reported to be the third leading source of fatal occupational inhalations in the US and the primary cause of work-related deaths among sewer workers (Bowker et al., 1985; Valent et al., 2002). In the 1980s-2000s numerous reports of fatal exposures to sulfide in connection with sewers or manholes have been reported in the US (Ballerino-Regan and Longmire, 2010; Dorevitch et al., 2002; Fuller and Suruda, 2000; Knight and Presnell, 2005; Snyder et al., 1995; Yalamanchili and Smith, 2008). But also in Europe in e.g. Spain (Nogué et al., 2011), Portugal (Matias et al., 2017a), Italy (Barbera et al., 2016), and France (Christia-Lotter et al., 2007) fatal consequences of sulfide exposure in connection to sewer systems have been reported. Most exposures are luckily not fatal and (Forsgren and Brinck, 2017) found that there is only about 5% or less mortality from H<sub>2</sub>S poisonings and the number seems to be dropping due to increased awareness and improved first-aid training.

Corrosion of sewer assets, both concrete structures and metallic parts, due to sulfides released to the sewer headspace is perceived to be the main cause of sewer deterioration (Apgar and Witherspoon, 2007; Jiang et al., 2016; USEPA, 1991b). It is a process where sulfuric acid is produced by microbial sulfide oxidation on moist surfaces above the waterline by bacteria of the genus *Thiobacillus* (Hvitved-Jacobsen et al., 2013). pH on the surface of pipe walls can drop significantly and has been measured in the range of pH 0.5-2 (Apgar and Witherspoon, 2007; Nielsen and Vollertsen, 2016). Chemical reactions between alkaline cementitious materials of the concrete sewer pipes and manholes with the produced sulfuric acid results in physical changes of the concrete structure. In this reaction gypsum is formed which does not provide structural support to concrete pipes (Davis et al., 1998). Corrosion rates of concrete has in different studies been reported to be in the range from 0.2-7.7 mm year<sup>-1</sup> depending on setup, pipe age, humidity, and exposure time (Jiang et al., 2016, 2014, Mori et al., 1992, 1991; USEPA, 1991a; Vollertsen et al., 2008; Wells and Melchers, 2015). Sewers are large-scale investments which in many cases have an expected design life of around 80 years (Kaempfer and Berndt, 1999). However, the loss of structural support of the pipes due to corrosion can significantly reduce the lifespan of the pipes, e.g. in British Columbia the service life was reduced to 30 years in a trunk sewer (Hewayde, 2005) or even to less than 10 years as reported by USEPA (1991a). Ultimately corrosion, if not taken care of, has been experienced to cause structural collapses (Matias et al., 2017a; Vasil'ev et al., 2013). Therefore, special consideration should be given to corrosion caused by sulfides.

### 1.3. COST OF SULFIDES IN SEWER SYSTEMS

Sulfide induced corrosion can reduce the life of assets of sewer systems, e.g. pipes, manholes and wet wells, to a significant extent. The corresponding asset depreciation and ultimately premature replacement or rehabilitation of structural components globally causes derived economic impacts of many billion dollars every year (Hvitved-Jacobsen et al., 2013; Jiang et al., 2015; Witherspoon et al., 2004).

Depreciation of assets can be difficult to estimate as sewer systems are underground structures not easy to inspect. Depreciation of sewer system assets is in Flanders, Belgium, approximated to amount to €5 million per year. This corresponds to approximately 10% of the cost spend for wastewater collection and treatment (Vincke, 2002). In Australia asset depreciation is estimated to be worth AU\$100 million per year (Gutierrez et al., 2011) and in the US the cost is estimated to US\$13.75 billion per year (Koch et al., 2002). With the loss of assets taking place, the inevitable rehabilitation sums to significant amounts. The cost for restoration of damages in public and private sewer networks, due to sulfide induced corrosion, is estimated to attain up to US\$20 billion in Germany, for complete rehabilitation of the system (Kaempfer and Berndt, 1999). In US repair and maintenance of sewer systems due to corrosion is estimated to be around US\$4.5 billion in 2003 with an estimated growth of 8-10% per year (Sterling et al., 2009), the market furthermore faces an

estimated backlog of US\$ 3.2 billion (Bowker et al., 1985). In Canada, pipe rehabilitation costs for two specific projects were in the order of US\$0.8-1.8 million km<sup>-1</sup> (Hewayde, 2005), and in US the estimates for rehabilitations are around US\$1.3-3.5 million km<sup>-1</sup> (Sydney et al., 1996; USEPA, 1991a).

Many water utilities have realized the problem and associated cost of depreciation and have initiated abatement strategies implementing different chemical and physical initiatives. Abating sulfides incur costs and depending on the severity of the problem, these costs might be comparable to the value of assets lost (Apgar and Witherspoon, 2007). But as rehabilitation cost can be significant it is often cost effective to perform chemical dosing to abate corrosion (Oviedo et al., 2012). Addition of chemicals for controlling odors in San Francisco has in fact become the preferred method of abatement, but also physical methods with off-gas control are being applied (San Francisco Public Utilities Commission, 2009). The cost of sulfide abatement is site specific and depends on which initiatives are taken, the proportions of the problem and to which sulfide level control is performed. In the city of San Antonio, Texas and at Gold Coast Water, Australia, chemical costs for single sewer lines attain roughly AU\$650.000 year<sup>-1</sup> and AU\$1 million year<sup>-1</sup> respectively (Gutierrez et al., 2011; Oviedo et al., 2012). In contrast hereto, Mariager Fjord Vand, Denmark, had chemical expenses of just US\$6000 year<sup>-1</sup> for odor control of a 3 km force main (Lyngsø et al., 2015). In 2005, collection system odor control in San Francisco attained a cost around US\$1-1.5 million year<sup>-1</sup> (San Francisco Public Utilities Commission, 2009), which is on a similar scale to spending's of the Sanitation Districts of Los Angeles County of around US\$2 million year<sup>-1</sup> in 1991 (USEPA, 1991a).

The issues with sulfide in sewer systems and the associated costs is likely to increase in the future. With water scarcity on the agenda many places, water savings and recycling will be encouraged. This will increase wastewater strength and decrease water volumes. Whilst still flowing in the old pipes, this will give longer retention times, as these are too large for the decreased volume. Additionally, the trend of centralizing wastewater treatment and increasing sewer system coverage will lead to wastewater being conveyed over ever longer distances. These factors summed together will increase the anaerobic retention in the systems and thereby also the potential for sulfide formation. With this follows also odors and corrosion of assets, thus increasing the problems that current systems experience (Apgar and Witherspoon, 2007; Barjenbruch, 2003; Tjandraatmadja et al., 2005).

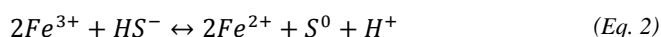
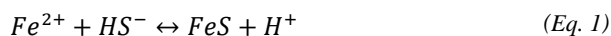
To overcome these challenges, conceptual sewer models have proven a valuable tool in aiding fundamental decisions on system management and planning (Vollertsen et al., 2015, 2011). This approach is not only valid for planning of new systems, but also existing systems where sulfide abatement needs to be implemented or operational practice needs to be corrected. The approach is already actively being used in preparation of sewer system master plans by e.g. the San Francisco Public Utilities Commission, who are giving special attention to odor control measures in sewer

systems (San Francisco Public Utilities Commission, 2009) and the Region of Peel in Canada that in its plans address both odors and corrosion (Andrews et al., 2008). Developing the understanding of in-sewer processes connected to sulfide abatement is therefore key to improve the models and get more reliable modeling output that can be used for decision making.

## 2. STATE-OF-THE-ART

### 2.1. SULFIDE PRECIPITATION

Chemical dosing is a commonly used method for control of sulfides, with iron salts being one of the preferred options (Ganigue et al., 2011; San Francisco Public Utilities Commission, 2009). Salts of ferrous and ferric iron can be used for this purpose. Ferrous sulfide (FeS) is formed directly in a reaction between ferrous iron ( $Fe^{2+}$ ) bisulfide (Eq. 1) (Pomeroy and Bowlus, 1946). Ferric iron ( $Fe^{3+}$ ) must first undergo a reduction to ferrous iron, which afterwards precipitates to form FeS. Reduction of ferric iron can be either chemically as described in (Eq. 2), where it is coupled with the oxidation of bisulfide to elemental sulfur, or biochemically by bacterial conversion (Hvitved-Jacobsen et al., 2013).



Precipitation of sulfides with iron salts in wastewater at both laboratory scale and in full-scale sewer systems has been studied for the last half-century (Jameel, 1989; Nielsen et al., 2008a; Padival et al., 1995; Pomeroy and Bowlus, 1946; Tomar and Abdullah, 1994; Zhang et al., 2010). Many of these investigations have been done from a stoichiometric point of view under different wastewater conditions, by varying pH, redox conditions, initial sulfide concentrations, etc. Other studies have focused on an assessment of the effectiveness between the two different iron species used individually or in combination.

### 2.2. IRON SALTS IN BIOFILMS

Addition of iron salts for sulfide abatement in sewers may beside sulfide precipitation also influence sewer biofilms. It has previously been demonstrated that cations can interact with constituents of the biofilm matrix, such as extracellular polymeric substances (EPS) which contains a vast amount of anionic groups or at the cellular level with walls, membranes, or cytoplasm (Flemming, 1995; van Hullebusch et al., 2003). These interactions can be through complexation or ion exchange, and furthermore surface precipitation may play a role (Li and Yu, 2014). It has been found that e.g. zinc, copper, cadmium and iron can accumulate in sulfate-reducing bacterial biofilms (Nielsen et al., 2005a; White and Gadd, 2000, 1998). On a weight basis, EPS has been shown to accumulate up to 25% of metal ions, but the specific amount scavenged will be influenced by pH, with a higher amount at near-neutral pH compared to acidic conditions due to a competition with hydrogen ions (Flemming, 1995). However, Nielsen et al. (2005a) found no correlation between EPS and metal concentration, which they ascribed to the fact that metal precipitation was the cause

of accumulation and not sorption to the biofilm matrix. This is in line with Liu and Fang (1998) who showed that cells of sulfate-reducing bacteria of granular sludge were coated by metal sulfides of copper, iron and nickel and that this layer probably was a cause of inhibition of bioactivities. Also several other authors have experienced inhibition of bacterial activity, which they ascribed to a similar mechanism where ferrous sulfide or other metal sulfide coatings of the cells act as barriers for reactants (Liu et al., 2001; Roden and Urrutia, 1999; Utgikar et al., 2002).

In activated sludge treatment ferric iron addition has been shown to increase floc strength and thereby enhance discharge quality of effluents. But when dissimilatory ferric iron reduction took place in anaerobic parts of the flocs, with conversion to ferrous iron, a deterioration and deflocculation of the flocs was observed (Caccavo et al., 1996; Nielsen and Keiding, 1998; Novak et al., 2001). How iron salt dosing effects sewer biofilms of force mains has not been investigated. However, considering the above it is reasonable to believe that it to some extent could have similar implications on the biofilms.

### **2.3. KINETICS OF SULFIDE PRECIPITATION**

Knowledge on kinetics of sulfide precipitation in wastewater is largely lacking and has not received the same attention as stoichiometry. This is probably because iron salts have been added to the start of the force main, where the subsequent retention of the iron amended wastewater has several hours of reaction time, and kinetics therefore has been considered irrelevant. It has however been believed that sulfide precipitation in wastewater with ferrous iron is a rapid process (Zhang et al., 2008). Nielsen et al. (2007) concluded that kinetics of the reaction could not be quantified by manual sampling, as they visually observed an instantaneous blackening of wastewater containing sulfide after addition of ferrous iron. FeS precipitation with ferric iron is assumed to be slower, as ferric iron must undergo a reduction to ferrous iron, before sulfides are precipitated (Hvitved-Jacobsen et al., 2013), however the initial reduction step might also remove sulfides as elemental sulfur but the kinetics of the total reaction has not been quantified in wastewater systems. Nielsen et al. (2005b) demonstrated that ferric iron was quickly reduced to ferrous iron when added to wastewater containing sulfide, and that sulfide precipitation subsequently proceeded for some hours, when measuring iron species and metal sulfide build-up.

In deoxygenated low ionic strength aqueous solution Harmandas and Koutsoukos (1996) investigated sulfide precipitation of equimolar concentrations of ferrous iron and sulfide in the range of 10-50  $\mu\text{M}$ , which corresponds to around medium sulfide concentrations found in municipal wastewater (Henze and Comeau, 2008). At near neutral pH conditions, Harmandas and Koutsoukos (1996) found that FeS in the form of Mackinawite formed, with higher initial concentrations of reactants yielding higher rates. In deoxygenated seawater, in a range of pH conditions corresponding to what could be expected in wastewater, precipitation of sulfides was measured using ferric



hydro(oxides), present in a ratio twenty times what would be required according to stoichiometry (Eq. 2) (Yao and Miller, 1996). The reaction was found to be overall second order, the reaction rate constant being pH dependent and elemental sulfur the dominant product formed during oxidation of sulfide. Yao and Miller (1996) furthermore found that phosphate and different inorganic ligands could increase or decrease the reaction rate constant by complex-binding the iron, an issue which also was discussed by Nielsen et al. (2005b) to influence the reaction rate.



### 3. OBJECTIVE

A concern of sewer assets, health issues and odor problems related to sulfides are driving odor and corrosion abatement in sewer systems around the world. Practical experiences and best practices exist when performing abatement of sulfide in force mains using iron salts. However, the influence of iron salts on the underlying processes within force mains, as well as the precipitation rate, are still largely unanswered. The aim of this study is therefore to investigate how iron salt dosing affects these issues.

To address this aim, the following research questions were put forward.

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**Research question 1:** Does precipitation of ferrous sulfide change the physical properties of force main biofilms?

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To answer this, diffusivity was measured *in situ* on biofilms under different flow regimes. The biofilms were grown in a pilot setup at conditions typical for force mains.

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**Research question 2:** Does ferrous and ferric iron addition influence the microbiome of sewer force main biofilms?

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To answer this, the microbiome of biofilms from force mains treated with iron was examined with respect to diversity and abundance of genera related to sulfide and methane production.

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**Research question 3:** Does addition of ferrous and ferric iron influence the activity of force main biofilms?

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To answer this question the activity of sewer force main biofilms subject to iron treatment was measured with emphasis on sulfide and methane production.

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**Research question 4:** Is the rate of sulfide precipitation using ferrous and ferric iron important to consider for end-of-pipe treatment?

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To answer this, the kinetics of sulfide precipitation was measured at different iron to sulfide ratios and at different pH conditions.



## 4. INFLUENCE OF FORCE MAIN BIOFILMS

Start-of-pipe abatement of sulfides has traditionally been the method of choice in force mains due to practical issues such as access to mains power and space for storage of chemicals. With this abatement strategy, chemicals such as iron salts are added before sulfides have formed in the force mains. Ferrous sulfide has a low solubility product constant and will readily precipitate in the reaction between sulfide and iron (Hvitved-Jacobsen et al., 2013). In force mains, sulfides are produced within the biofilm. The biofilms must be assumed to be fully penetrated by the iron added to the wastewater, and an accumulation of metal sulfides inside biofilms has correspondingly been observed (Nielsen et al. 2005).

The effect of treatment with ferrous and ferric iron, on biologically and physical interactions with the biofilms, has not been subject to studies in force mains with shear stress conditions comparable to real force mains. These interactions might ultimately have implications for conceptual sewer models, where an influence on sulfide production caused by addition of abatement chemicals are not accounted for. To close this knowledge gap Kiilerich et al., 2018b (**Paper III**), 2018c (**Paper IV**) and 2018d (**Paper V**) investigated the influence of ferrous and ferric iron treatment on force main biofilms.

### 4.1. METHODOLOGIES FOR STUDYING BIOFILM INTERACTIONS

Influences on sewer force main biofilms were studied in a combination of *in situ* and laboratory experiments. All experiments were conducted using mature steady state biofilms adapted to ferrous or ferric iron treatment. Biofilms were grown in a sewer system consisting of three identical force mains operated in parallel. The force mains were continuously fed with fresh municipal wastewater in an operational pattern mimicking conditions of real force mains. One force main worked as an untreated control, while the two other mains were treated with commercial available ferrous and ferric iron products. Products that are routinely applied in the water industry for abatement of sulfides. The iron salts were fed directly into the force mains during operation, at flows giving identical iron to sulfide ratios for the two treated lines. Estimation of sulfide concentrations in the force mains were done by calculating the sulfide formation rate using the empirical equation proposed by Nielsen et al. (1998), and with physical and operational data from the system. The force mains were constructed so they could be dismantled at 0, 100 and 200 meters, from the point of complete mixing of chemicals. At these positions along the force mains, biofilm sampling for activity measurements under laboratory conditions and microbiome analysis could be performed. Moreover, special designed units were inserted here, for conducting *in situ* diffusivity measurements of biofilms under conditions realistic for sewer force mains. These units could furthermore be isolated, completely filled with

anaerobic wastewater, and taken out of the system for analysis, while maintaining realistic hydrated biofilm conditions.

## 4.2. INFLUENCE OF IRON TREATMENT ON BIOFILMS

It was evident from the different experiments carried out, that iron salt induced physical changes of the force main biofilms. A distinct buildup of iron and sulfur in the biofilms of the iron-treated mains was observed. These two elements accumulated to an extent which exceeded the stoichiometric ratio of ferrous sulfide. The visual appearance of the biofilms was completely black, which indicates that the accumulation to some extent was composed of ferrous sulfide. The accumulation of ferrous sulfide inside the biofilms changed the texture of the biofilms compared to the untreated main. The biofilms of the untreated main had a slimy feel, whereas the iron treated biofilms had a more grainy-like feel, and these biofilms furthermore got optical opaque.

### 4.2.1. DIFFUSIVITY OF BIOFILMS

The physical changes of the biofilms were also evident in the measured differences in diffusivity. The ferrous and ferric treated biofilms both exhibited lower diffusivities than the untreated biofilm under the shear stresses applied. The biofilm model developed to approximate diffusivities gave decent fits to experimental data from the untreated and ferrous treated mains. Model fits to experimental data of the ferric treated biofilm were on the other hand poor. The poor fits of the model were because the conductivities measured during experimentation evened out well before they got close to the expected equilibrium conditions. This effect might even have resulted in overestimation of the diffusivities in the ferric treated biofilm, when the model fits were inspected carefully.

The hindered diffusivity in the biofilms of the ferric treated main could be coupled to a decreased amount of calcium, which was measured in the biofilms of Kiilerich et al. (2018b)(**Paper III**). The decrease in calcium was probably a direct result of the ferric iron addition, as  $\text{Fe}^{3+}$  can substitute calcium ions in bridging EPS of the biofilm matrix. This would in the first place stabilize the biofilm matrix, as  $\text{Fe}^{3+}$  EPS bindings, are stronger than the  $\text{Ca}^{2+}$  EPS bindings (Li et al., 2012; van Hullebusch et al., 2003). But as sulfide is formed in the biofilms,  $\text{Fe}^{3+}$  is reduced to  $\text{Fe}^{2+}$  in the reaction with sulfide. This reduction of ferric iron inside biological matrices has previously been shown to cause destabilization (section 2.2). This destabilization could then cause a structural collapse of the biofilm matrix or make it more susceptible to flow compression, which then will increase the resistance to diffusivity. A similar effect was not observed in the ferrous treated biofilms, where ferrous sulfide also formed. The difference was supposedly because ferrous ions in the first place cannot substitute calcium ions for binding to EPS. This is substantiated by the finding that the calcium content in the ferrous treated biofilm was equal to the content of the untreated biofilm.

Consequently, the calcium ions remained bound to the biofilm matrix, providing stability. The decreased diffusivity in the ferrous treated biofilms compared to the untreated biofilms, was instead ascribed to the physical effect of iron and sulfur accumulation onto or within the biofilm matrix.

A decrease in diffusivity will affect transport of substrates and products from the bulk wastewater and into the biofilms, as well as inside the biofilm. In the ferric treated line the decreased transport of molecules might have been further enhanced, as ferric iron can precipitate phosphate in liquid matrices such as wastewater and seawater (Metcalf and Eddy, 2003; Poulton et al., 2002), and moreover the present study showed that it precipitated soluble COD in the force main. A reduction of these compounds in the bulk wastewater will influence their availability within the biofilms.

The precipitation of COD might be brought about by the addition of the acidic ferric iron solution to the wastewater at circumneutral pH. Under these conditions ferric iron will rapidly precipitate to form flocs of amorphous or microcrystalline ferric (oxy)hydroxides (Cooper et al., 2003; Davydov et al., 1998), which then can induce flocculation and hence a reduction of the COD as observed in the study. This corresponds well with observations done during sampling, where fluffy orange-brown flocs were observed to be suspended in the ferric treated wastewater and after sedimentation a clearer water phase was seen compared to the untreated and ferrous treated samples. Some of the formed precipitates might also have deposited on the surface of the sewer biofilms in the ferric treated line, which will have increased the resistance of diffusivity further.

#### **4.2.2. BIOFILM MICROBIOME**

Competition for substrates between microorganisms within biofilms affects its populations. Due to altered availability in the amount of different electron donors and acceptors in the iron treated biofilms, this could give rise to different communities. The microbiomes of the three biofilms were in fact observed to be significantly different between the mains. These differences were observed both the microbial as well as on the functional level. However, whether above was the exact cause of microbiome separation observed between the three lines, cannot be deduced directly from this study.

Differences in the microbiomes were apparent at genus level and it was observed that presence and abundance of sulfide and methane producing microorganisms differed between the mains. Even though ferric iron was added to one of the mains, the only genus capable of ferric reduction detected in the microbiome was *Sulfurospirillum*. However, this genus was also present in the two other mains, and is beside ferric iron known to be able to utilize electron acceptors such as sulfite, sulfur and nitrate. The redox increase by addition of ferric iron thereby seemed unused by the microorganisms and sulfate respiration probably proceeded unhindered. The lack

of ferric reducers also indicates that the reduction of ferric to ferrous iron was a purely chemical reaction within the force mains.

Beside the differences between the three lines, a longitudinal diversity within each line was observed over the 200 meters studied. This might be due to the spatial variability in available substrates present along a force main (Rudelle et al., 2016) as the wastewater gets degraded during retention in the main. The force mains studied were rather short compared to real force mains. Hence the separation of the microbiome could potential increase or maybe even converge further down the line.

#### **4.2.3. ACTIVITY OF BIOFILMS**

The general activity of sewer biofilms from the two force mains subjected to iron treatment was found to be reduced compared to the untreated main. The reductions could not be caused by differences in diffusivities of the biofilms, which was demonstrated in-situ in the force mains, as biofilms prior to activity measurements were homogenized and kept in suspension during the experiments.

The difference in activity could possibly be due to differences in microbiomes of the three lines. Different microorganisms have different substrate preferences and if the substrates offered during experimentation were not optimal, the activity would be reduced. However, this is less likely as both of the iron treated lines were affected in a similar manner and these biofilms had significantly different microbiomes. Another possible explanation for the decreased activity of the ferrous and ferric treated biofilms could be that iron sulfides precipitated on the surface of the microorganisms (section 2.2) which would have affected e.g. their substrate uptake and thus their metabolic rates. This effect has also previously been believed to be the explanation for a decrease in activity of sewer biofilms, in a simulated laboratory scale force main treated with ferric iron (Zhang et al., 2009).

The above findings show that iron treatment of wastewater force mains for sulfide abatement, besides precipitation of sulfides, also influence the biofilms in physical, biochemical and microbiological manners. This implies that the added iron might have contributed to sulfide abatement by more than simply precipitation. Even though ferrous and ferric iron induced a comparable decrease in activity of the biofilms, ferric iron might be the best choice for start-of-pipe sulfide abatement as it also impedes diffusivity significantly. Furthermore, the advantages of ferric iron compared to ferrous iron, is the fact that ferric precipitates COD and phosphates in the wastewater. This might limit availability within the biofilms and thus reduce sulfide and methane production negatively.



## 5. PRECIPITATION KINETICS

In some sewer systems, start-of-pipe abatement of sulfides is infeasible or impractical and hence end-of-pipe abatement must be applied. This situation could e.g. occur in branched pressurized systems, where slugs of wastewater arrive from side branches into the main line. These slugs are conveyed further down the sewer line to the discharge point in a distinct plug-flow manner without being mixed with abatement chemicals dosed to the main line.

However, when applying end-of-pipe abatement, knowledge of kinetics for sulfide conversion is key. In wastewaters, the precipitation of sulfide is generally believed to be fast (Zhang et al., 2008), but kinetics of the sulfide precipitation has never been reported. In conceptual sewer models, precipitation of sulfides with iron salts has been assumed instantaneous (Hvitved-Jacobsen et al., 2013). Consequently, these models are, of today, not applicable as a design tool to decide the required location of end-of-pipe abatement installations in order to ensure sufficient reaction time for proper sulfide conversion. To close this knowledge gap Kiilerich et al., 2017 (**Paper I**) and 2018a (**Paper II**) investigated kinetics of sulfide precipitation using ferrous and ferric iron in anaerobic wastewater.

### 5.1. METHODOLOGY FOR STUDYING KINETICS OF SULFIDE PRECIPITATION

Precipitation of sulfides were investigated using two different setups. A time independent setup where a semi-steady state of precipitation was established (Kiilerich et al., 2017 (**Paper I**)), and a time dependent setup (Kiilerich et al., 2018a (**Paper II**)), where sulfide precipitation was followed over time. Both setups were run under deoxygenated conditions mimicking settings of wastewater at the end of a force main prior to depressurization.

The time independent setup utilized a plug flow methodology. In this setup sulfide containing waters and a ferrous iron solution was pumped in two separate tubes to a T-junction where quick mixing took place. The plug of mixed reactants was then conveyed to the measurement point, which, depending on the tube length and the respective pump flow, decided the specific reaction time of the semi-steady state precipitation measurement. This approach canceled out any initial mixing and sensor response times making it possible to measure a reaction time down to 1.5 seconds. In the time dependent setup, a completely mixed batch reactor was utilized. Here ferrous or ferric iron was added to a batch of sulfide amended water, and the disappearance of sulfide as a surrogate for precipitation was followed over time. Measurements from this setup needed to consider mixing time in the batch reactor and hence could not be used to measure reaction times below 6 seconds.

Precipitation of sulfide were in both setups followed using an online amperometric sulfide microsensor with a tip size of 500  $\mu\text{m}$ . This approach was used because off-line measurements applying chemical quantification was not possible as the precipitation reaction would proceed during sampling and preparation. The microsensor applied was a Clark-type electrode that measures the dissolved protonated form of sulfide. Concomitant measurements of pH were therefore performed and based on these measurements total sulfides could be calculated.

## 5.2. RESULTS OF SULFIDE PRECIPITATION

Even though results of precipitation obtained using the two setups are not directly comparable due to different methodologies, some analogies can be drawn. In contrary to what was expected from literature (Hvitved-Jacobsen et al., 2013; Zhang et al., 2008), both studies showed that precipitation of sulfides with ferrous iron was not taking place instantaneously, and that a time scale of minutes was needed to obtain proper sulfide conversion. It was furthermore found that ferric iron exhibited a faster reaction rate, even though it first must have undergone conversion to ferrous iron before precipitation could have taken place. However, the initial reduction step of the ferric iron, where sulfides according to (Eq. 2) are oxidized to elemental sulfur, will have increased the observed reaction rate constant, as measurements were done directly on sulfides and not on the formed ferrous sulfide. The reaction rates will hence have included both the formation of elemental sulfur and precipitation.

It was clear from both studies that pH influenced precipitation of sulfides, and at conditions where pH was below neutral, the efficiency of the added iron was poorest. This is not surprising as previous studies have shown that at decreasing pH an increase in stoichiometric ratio was needed to obtain proper conversion and below pH 6.5 iron salts are ineffective for sulfide precipitation (Boon, 1995). For the time-independent study this was reflected in a high stoichiometric ratio between ferrous iron and sulfide compared to equilibrium modelling, and a resulting poor conversion of the sulfides at the tested reaction times. In the time-dependent study, this was reflected in the reaction rate constant and thus the resulting half-life, which increased with decreasing pH for both ferrous and ferric iron addition.

The iron to sulfide ratio applied in the experiments did also influence precipitation of sulfides to some degree, but the effect was only statistical significant for ferrous iron. At an increasing ratio the reaction half-life of sulfide precipitation decreased. Additionally, an excess of ferrous iron was needed to ensure complete conversion of sulfides, as an amount of unreacted sulfide was observed at low ratios. The amount of sulfide left at equilibrium was also influenced by pH, and a combination of a pH above neutral conditions and a high ferrous to sulfide ratio gave the best conversion. Ferric iron in contrary precipitated all sulfides equally well over the range of pH and ratios tested. This implies that to obtain proper sulfide control (half-life and conversion) using ferrous iron both pH and the ratio must be considered,

whereas for ferric iron only pH is important to keep under control while minimizing the ratio.

The wastewater matrix was demonstrated to influence precipitation to some extent. However, the exact contribution did not seem to correlate directly with the concentration of soluble COD in the time-independent setup. The influence of the different sampling sites varied according to the reaction times tested, with one type being statistically significant at one reaction time while not at another. Whether this was due to more specific components within the matrix was not investigated further. For the time dependent setup, precipitation using ferrous iron was not influenced statistically significant by wastewater type. In contrary to this, precipitation using ferric iron was found to be influenced by wastewater type. This was evident from the correlation analysis where the calculated reaction rate constant was negatively correlated to COD, thus an increased COD content would yield a decreased reaction rate constant. This effect was not caused by phosphates present in the matrix as these had been accounted for in the ferric to sulfide ratio. Instead it would probably originate from a precipitation of organic matter present, which in Kiilerich et al. (2018b)(**Paper III**) was shown to take place. A precipitation of organic matter would then utilize some of the ferric iron present which could not be used for sulfide precipitation. Hence the effective ratio of ferric to sulfide would be reduced, which most probably was included in the measured reaction rate constant.

In the experiments, sulfide precipitation was examined at sulfide concentrations in the range between 165-495  $\mu\text{M}$ . These conditions correspond to wastewater with a high concentration of sulfide, where derived problems in the sewer system will be seen if not handled (Henze and Comeau, 2008; Hvitved-Jacobsen et al., 2013). Whether the results can be extrapolated to lower sulfide concentrations has not been investigated in this study, but could be subject to further experimentation as (Harmandas and Koutsoukos, 1996; Poulton et al., 2002) report that the initial ratio in aqueous solution has an impact on precipitation.

From these findings it has been demonstrated that precipitation kinetics of sulfide should be taken into account in end-of-pipe abatement strategies using iron salts. It was also shown that the precipitation rate to some extent could be controlled by adjusting pH and the iron to sulfide ratio. The overall rate constant for sulfide precipitation was found to be approximately second order for both ferrous and ferric iron. Model equations for calculation of kinetic rate constants and the remaining sulfide concentrations at equilibrium at different iron to sulfide ratios and pH conditions were proposed in Kiilerich et al. (2018a)(**Paper II**).



## 6. RECOMMENDATIONS ON SULFIDE ABATEMENT STRATEGIES

It is well-known that both start-of-pipe and end-of-pipe abatement can be used for sulfide abatement in the force mains of sewer systems in order to minimize assets depreciation, decrease odors, and lower health risks. Which specific strategy to apply depends among other things on system layout, access to mains power, and physical space at the location of deployment.

As shown in this study, a benefit of start-of-pipe abatement is that the iron added, besides precipitation of sulfides, will induce an overall reduction of activity throughout the main, through a combination of microbial and physical alterations of the biofilms. However, adding iron in the correct amount is notoriously difficult as both flows and loads of wastewater change constantly. The experienced inhibition of the biofilms is also not fully quantifiable. This implies that manual control of chemical dosages is unsuitable. Instead automated dosing algorithms that can respond to the changing conditions should be applied. These algorithms can adjust dosage according to e.g. the specific inhibition of sulfide production experienced in the main. But even when using automated algorithms, complete abatement cannot be guaranteed at all times. Predictions of temporal variations in wastewater flow and characteristic as well as the specific inhibition of a future state of the system is not a trivial case if not impossible. However automated control algorithms are gaining interest despite the drawbacks and have recently been proven to optimize dosage, at least when seen from a perspective of chemical savings (Barjenbruch, 2003; Ganigué et al., 2018; Liu et al., 2013; Lyngsø et al., 2015).

End-of-pipe treatment does not induce any beneficial inhibitory changes to the biofilms. Chemicals are applied just in time for complete sulfide conversion to take place before discharge. The location of the injection point to allow the needed reaction time can be decided based on the model for sulfide precipitation proposed in Kiilerich et al. (2018a)(**Paper II**). It can furthermore be evaluated whether an additional pH correcting dosing should be applied, to tune the reaction time to obtain the required sulfide control within a predefined distance between addition and depressurization.

In contrary to start-of-pipe treatment the advantage of end-of-pipe treatment is that the specific amount of sulfides to precipitate in the wastewater in principle can be measured online (Sutherland-Stacey et al., 2008). The unpredictable changing flow and load conditions in the force main, resulting in changeable sulfide concentrations, can thereby be ignored. According to the measured sulfide, the exact amount of iron can be added via a simple automated control loop, thus ensuring proper sulfide conversion at all times.



## 7. CONCLUSIONS

The aim of this study was investigated through four research questions and the following conclusions were drawn.

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**Research question 1:** Does precipitation of ferrous sulfide change the physical properties of force main biofilms?

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It was found that addition of ferrous and ferric iron for sulfide precipitation in wastewater affected the diffusivity of force main biofilms. Ferric iron treatment caused the greatest decrease in diffusivity, which was proposed to be due to biofilm instability.

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**Research question 2:** Does ferrous and ferric iron addition influence the microbiome of sewer force main biofilms?

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Microbiomes of sewer force main biofilms were found to differ significantly according to whether the main was untreated, treated with ferric or treated with ferrous. Differences were detected on the microbiological as well as on the functional level of the microbiomes. Beside differences between the force mains, a longitudinal difference of microbiomes on each of the mains were also observed.

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**Research question 3:** Does addition of ferrous and ferric iron influence the activity of force main biofilms?

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A general inhibition of biofilm activities when previously treated with ferrous and ferric iron was found in batch experiments of suspended biofilms. The influence could not be ascribed to the difference in redox potential between the iron salts, as only one ferric reducing genus was identified. The difference was instead thought to be physical due to the precipitation of ferrous sulfide.

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**Research question 4:** Is the rate of sulfide precipitation using ferrous and ferric iron important to consider during end-of-pipe treatment?

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It was found that sulfide precipitation using ferrous and ferric salts was not instantaneously as previously assumed, and must consequently be considered during end-of-pipe treatment. The fastest precipitation rates were found when applying ferric iron. Moreover, it was demonstrated that rates depended on pH and the iron to sulfide ratio when using ferrous iron, whereas pH was the only controlling parameter using ferric iron.

Translating the conclusions of this study into practical applications, to some extent relate to implementation into conceptual sewer models. Improved models will help in planning mitigation of the consequences ascribed to sulfides in real life sewer systems. Findings of this study relates to estimation of sulfide production in force mains treated with iron salts. Even though the specific inhibition of the biofilm processes due to iron treatment was not specifically quantified, a reduction in

production should be accounted for in the models to obtain more reliable results. Also in planning of sulfide abatement using an end-of-pipe strategy, results obtained in this study can be beneficial. Model equations were proposed for calculation of kinetic rate constants of sulfide precipitation in a range of pH and iron to sulfide ratios typical for wastewater. These model equations can be readily implemented into the sewer process models, which will aid in deciding location and configuration of an abatement station.



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