Kinetics of sulfide precipitation with ferrous and ferric iron in wastewater
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ABSTRACT
Traditionally, sulfide abatement has been done by adding e.g. ferrous or ferric iron salts to the start of sewer force mains. Iron dosage must hence correspond to an estimate of how much sulfide will form while the wastewater stays in the main, which is not straightforward. Adding iron salts at the end of the main has the advantage that the exact amount of sulfide to precipitate, in principle, can be known. A drawback is that the reaction time is short compared to start-of-pipe treatment. Sulfide precipitation rates and the concentration of sulfide left after the process had run to completion were measured using an online hydrogen sulfide probe to resolve the fast precipitation reaction. Experiments were conducted in anaerobic wastewaters spiked with sulfide, and carried out under different pH conditions and with various iron-to-sulfide ratios. Sulfide precipitation rates were demonstrated to be faster with Fe(III) than with Fe(II). Experiments furthermore showed that for Fe(III), pH was the controlling parameter, whereas for Fe(II) both pH and the iron-to-sulfide ratio were important. Proposed are model equations to predict variables for the rate equations, which can be adopted by practitioners dealing with sulfide abatement.

Key words | force mains, odor control, reaction rates, sewerage, sulfide abatement

INTRODUCTION
Wastewater collection systems convey sewage from water consumers to treatment works upon which the treated water is discharged to a recipient. Full-flowing force mains are an inevitable part of any such system, either to lift the water from one level to another or to force it over long distances. In the latter case, the wastewater commonly stays in the main for hours. Wastewater is highly biologically active, and bacteria in the wastewater, the sewer biofilms, and the sediments rapidly consume any initially present oxygen. Anaerobic heterotrophs such as fermenters and sulfate reducers then take over, with the activity of the latter leading to formation of sulfide. This sulfide builds up in the sewage and is partly released from it when the wastewater depressurizes at the end of the main, for example in transfer shafts or at the inlet to the treatment works. From here, sulfide gas might escape to the surroundings where it gives rise to a foul smell. Besides being malodorous, sulfide is extremely toxic and causes corrosion on moist metal and concrete surfaces, which can reduce the service life of the sewer assets significantly and lead to the premature failure of components (Boon 1995).

To counteract the formation of sulfide and hence the nuisances it brings, different abatement strategies are used, for example the addition of oxygen or nitrate for maintaining high redox conditions, the addition of hypochlorite for chemical oxidation, or the addition of iron salts for precipitation (Hvitved-Jacobsen et al. 2013). Addition of iron salts to the sewage for sulfide control has proven effective and is a common and well-documented practice where sulfide is removed as insoluble iron sulfide. Iron, as either ferrous (Fe(II)) or ferric (Fe(III)), or a mix of these, has been used for the purpose. Which is the most effective for sulfide control in sewage is not agreed upon in literature and the discrepancies may be ascribed to variations in sewage characteristics and experimental procedures (Jameel 1989; Padival et al. 1995; Ganigue et al. 2011).

Ferrous iron precipitates directly with bisulfide (HS⁻) as ferrous sulfide (FeS) (Equation (1)). Ferric iron is, on the other hand, proposed to have an additional reaction step, as it needs to be reduced to ferrous iron before it precipitates sulfide, as in Equation (1). This reduction can either take place chemically during the oxidation of bisulfide to
elemental sulfur ($S^0$) (Equation (2)) (ASCE 1989), or biochemically, where the oxidation power is utilized by a specific group of chemoautotrophic bacteria for respiration (Hvitved-Jacobsen et al. 2013).

$$Fe^{2+} + HS^- \leftrightarrow FeS + H^+ \quad (1)$$

$$2Fe^{3+} + HS^- \leftrightarrow 2Fe^{2+} + S^0 + H^+ \quad (2)$$

Traditionally, and for practical reasons, iron is added directly into the pump sump or at the start of the force main, before sulfide has formed (Ganigue et al. 2011). This implies that iron must be added in an amount that corresponds to the sulfide that will be produced during transport in the main. However, the sulfide formation prediction is rather uncertain, as parameters influencing it, e.g. retention time, concentration of biodegradable matter, temperature, pH, etc., may vary substantially in a short timescale (Gudjonsson et al. 2002; Hvitved-Jacobsen et al. 2013). Further complicating the prediction is the fact that the observed stoichiometric requirement does not follow Equations (1) and (2). In practice, the required stoichiometry depends on both the initial sulfide concentration, pH, and wastewater constituents to a degree, which today is only partly understood (Boon 1995; Firer et al. 2008; Nielsen et al. 2008, 2005).

In addition, the physical layout of the sewer system can complicate start-of-pipe treatment. In branched force mains, the plug flow hydraulics of the network results in sewage plugs from branch lines not mixing properly with sewage in the main line. This implies that chemicals dosed to the main line do not mix into sewage from the branch lines. To obtain proper abatement in these systems with start-of-pipe treatment, a dosing point must be established at every pumping station of the pressurized system. An alternative approach, and for some sewer systems the only practical solution, is to place the dosing point at the end of the force main prior to depressurization. With this approach, the exact amount of sulfide to be abated can in principle be measured, hence a precise amount of iron chemicals can be added to the sewage passing the dosing point. This approach was, in recent studies, shown to be viable for nitrate dosage in a laboratory setup simulating a force main, and furthermore it proved to optimize dosing compared to traditional start-of-pipe addition (Gutierrez et al. 2010).

Performing abatement at an end-of-pipe location implies that the reaction kinetics and stoichiometry should be understood, so complete sulfide conversion can be ensured before the sewage depressurizes. Even though the stoichiometry of sulfide precipitation using both ferrous and ferric iron has been extensively studied, the kinetics of the precipitation in sewage applications has not received the same attention. Without being more specific about the rate, Zhang et al. (2008) state in their review that sulfide precipitation using ferrous iron is rapid. Findings of Nielsen et al. (2007) agree with this statement, as they judged visually and without further quantification, that ferrous sulfide precipitation happened almost instantaneously after the addition of ferrous iron to sewage containing sulfide. They furthermore concluded that the kinetics of the reaction could not be qualified by manual sampling techniques.

It is generally believed that ferrous iron reacts faster than ferric iron, as ferric iron first must undergo a reduction to ferrous iron before sulfide precipitation can take place (Hvitved-Jacobsen et al. 2013). In Nielsen et al. (2005) it was shown that that ferric iron added to anaerobic sewage in the presence of sulfide underwent a fast reduction to ferrous iron, and that the subsequent precipitation with sulfide continued for a couple of hours. This implies that the first step of the reaction probably is chemical. However, this statement was not specifically investigated. The observed sulfide oxidation of the complete reaction in Nielsen et al. (2005) came close to what would be expected from Equation (2), where elemental sulfur is formed using sulfide as the electron donor for the ferric reduction instead of organic matter. However, in activated sludge flocs where sulfide only is present in low concentrations, it has been shown that the biochemical pathway for ferric reduction is followed (Rasmussen & Nielsen 1996).

In a study quantifying the reaction time for sulfide precipitation using ferrous iron at plug flow conditions, Kiilerich et al. (2017) showed that the precipitation reaction, in buffered water and sewage under different pH conditions and at various molar ratios of ferrous to sulfide, did not run to completion within 30 seconds. This conclusion was based on the high stoichiometric ratio and poor conversion of the sulfide observed at the measurement point. This demonstrates that sulfide precipitation is not instantaneous and kinetics must be considered when performing end-of-pipe treatment. A similar conclusion of considering precipitation kinetics was also drawn in the study of Nielsen et al. (2005), where ferric iron was used for precipitation.

The present work attempts to contribute to understanding the kinetics of sulfide precipitation using ferrous and ferric iron. The precipitation kinetics and related stoichiometry is investigated in buffered water and sewage under different pH conditions and various iron-to-sulfide ratios.
These findings are used to derive empirical equations describing the rates of precipitation, which can be implemented in the design of sulfide abatement installations and in conceptual sewer models. While the latter, a decade ago, was more an academic exercise than a practical tool, sewer process models are today increasingly used by the industry to, amongst other things, design sulfide abatement strategies (Vollertsen et al. 2015).

MATERIALS AND METHODS

Kinetics of sulfide precipitation using ferrous and ferric iron was investigated in buffered water free of organic matter and wastewaters obtained from three different locations. A laboratory scale batch reactor was used and the processes studied under anaerobic conditions in varying pH conditions (6.5, 7.0, 7.5 or 8.0) and iron-to-sulfide ratios close to or slightly above stoichiometric requirements (0.81 to 2.49 μM Fe(II) (μM S(-II))⁻¹ (n = 44) and 0.71 to 3.22 μM Fe(III) (μM S(-II))⁻¹ (n = 49)).

Buffered water was freshly prepared by dissolving Na₂CO₃ in MilliQ water (18 MΩ cm⁻¹) to a carbonate alkalinity of 4.05 meq L⁻¹, and NaH₂PO₄·2H₂O to a phosphate concentration of 105 μM for the experiments using ferrous iron. The ferric iron experiments were conducted in buffered water having 13.5 meq L⁻¹ of carbonate alkalinity and 63 μM of phosphate concentration.

Three different municipal wastewaters which represented fresh, medium-fresh, and old wastewater were tested. Fresh wastewater was collected in the town of Frejlev in Denmark, where the retention time from source to the sampling point does not exceed half an hour. The wastewater is well oxygenated at the sampling point, as the drainage area is steep. Medium-fresh wastewater was collected in the town of Svenstrup in Denmark. This drainage area is larger and shallower and wastewater is transported to here in intercepting force mains from several small towns in the surroundings. This results in wastewater of mixed ages that is less oxygenated. Old wastewater was collected at Aalborg West wastewater treatment plant (WWTP), Aalborg, Denmark. This WWTP receives wastewater from outlying towns, together with wastewater from the city of Aalborg itself. Wastewater sampled from this point was the least oxygenated and had the longest retention time. Depending on concentration range Hach Lange chemical oxygen demand (COD) cuvette test kits LCK314 and LCK514 (Hach Lange GmbH, Düsseldorf, Germany) were used to determine the total and dissolved COD of the different wastewaters. Samples for dissolved COD were filtered through a Sartorius GF + CA 0.45 μm filter prior to loading into the cuvette kit. Phosphate and carbonate alkalinity of the wastewaters were measured using the protocols described in Dansk Standard (1996) and Eaton et al. (2005).

Experimental setup

Experiments were conducted in a cylindrical glass reaction vessel fitted with a polyoxymethylene lid. The reaction vessel contained 940 mL of liquid. The reactor was placed on a magnetic stirrer and the content stirred constantly during the experiment. Probes for online measurement were inserted through the lid of the reactor. Complete mixing in the reactor was measured to be achieved after 6 seconds. This time limit was determined by injecting Rhodamine B into the reaction vessel containing water stirred at the same intensity which was used for the experiments. The time to reach steady state light absorbance of Rhodamine B was measured at 555 nm.

Hydrogen sulfide was measured online (data collected s⁻¹) using a Unisense Sulfide Gas Minisensor 500 μm (H₂S-500) coupled with a Unisense Multimeter (Unisense A/S, Aarhus, Denmark). The sulfide sensor only measures the unionized sulfide, and a calculation of total sulfide could be done using accompanying measurements of pH. pH measurements were obtained online (data collected s⁻¹) using a Radiometer Analytical PHC2001-8 Combination Red-Rod pH Electrode coupled with a Radiometer Analytical PHM210 standard pH meter, MeterLab® (Radiometer Analytical SAS, Villeurbanne Cedex, France) and data collected with a proprietary data acquisition program. Oxygen was measured with a PreSens Fibox 3 fiber optic oxygen meter and an oxygen sensitive optode (PreSens GmbH, Regensburg, Germany). Temperature data were acquired every 15 min using a digital thermometer (Ludwig Schneider GmbH, Wertheim, Germany). Prior to use, sensors were calibrated as described in the manuals.

Buffered water or wastewater samples were deoxygenated by flushing high-purity nitrogen gas (5.0) directly into the reactor vessel. When all traces of dissolved oxygen were removed, the reactor was immediately sealed off with the lid, ensuring there was no headspace above the liquid. Ingress of oxygen to the system during an experimental run was by initial tests found to be negligible. Sulfide was added to the target concentration from a 40 mM stock solution (Na₂S·9H₂O crystals dissolved in deoxygenated MilliQ water), and pH adjusted to the desired level in the reactor with hydrochloric acid and sodium hydroxide.
After steady state conditions had been established in the reactor, a baseline of pH and sulfide were recorded. Subsequently, the desired iron-to-sulfide ratio was obtained by adding either ferrous iron from a freshly prepared 80 mM stock solution (Anhydrous FeCl\textsubscript{2} dissolved in 2 mM deoxygenated HCl) or ferric iron (FeCl\textsubscript{3}) from a 3.55 M PIX111 solution (Brenntag Nordic A/S, Ballerup, Denmark).

In water treatment, it is well-known that ferric iron precipitates with phosphate (Snoeyink & Jenkins 1980). To account for the ferrous iron used for phosphate precipitation, the concentration of dissolved phosphate was measured before the addition of ferric iron and again after the termination of the experiment. Samples were prepared by filtering through a Sartorius GF + CA 0.45 μm filter before measurement was carried out using Hach Lange phosphate cuvette test kits. Depending on the concentration range LCK349 and LCK350 were used.

**Deriving kinetic parameters**

At each experimental run, the concentration of total dissolved sulfides was calculated based on the measured unionized sulfides and the concomitant pH value. A baseline of the total sulfide concentration ([S(-II)\textsubscript{0}]) was determined by root mean square error (RMSE) fitting of data acquired before ferrous or ferric iron were added. Promptly after the addition of iron, the sulfide concentration declined in a hyperbolic manner. The initial stoichiometric ratio (ratio\textsubscript{init}) for each specific experiment was calculated according to Equation (3).

\[
\text{Ratio}_{\text{init}} = \frac{[\text{Fe}_\text{II}]}{[\text{S}(-\text{II})\text{0}]} \quad (3)
\]

where [Fe\textsubscript{II}] is the molar concentration of Fe(II) or Fe(III) at time \( t = 0 \) (μM Fe), with Fe(III) being corrected for the amount lost to phosphate precipitation as measured and assuming a reaction stoichiometry of \( \text{Fe}^{3+} + \text{PO}_4^{3-} \rightarrow \text{FePO}_4 \). Accordingly, \([S(-II)\text{0}]\) is the concentration of total dissolved sulfide at time \( t = 0 \) (μM S).

Concentrations are used for the calculations, instead of activities of the species. This is done as the ionic strength of the buffered water at initial conditions was 0.01 M and 0.045 M for the reactions using Fe(II) and Fe(III), respectively. According to prediction by Visual MINTEQ ver. 3.1 (Kungliga Tekniska Högskolan, Stockholm, Sweden), the ionic strength at equilibrium is 0.007 M for the Fe(II) and 0.016 M for the Fe(III) experiments. Wastewater from Frejlev was estimated to be in the range of 0.02 M, based on conductivity measurements and following conversion according to Snoeyink & Jenkins (1980). Using concentrations is justified, as the activity coefficient of divalent cations and anions is approximately equal at these ionic strengths (Snoeyink & Jenkins 1980), and the activity coefficients in the following calculations hence will cancel out. In the reactions using Fe(III), precipitation would have been a combined effect of both Fe(II) and Fe(III), hence an exact activity coefficient cannot be determined. Precipitation of sulfide using Fe(II) can be described using rate Equation (4).

\[
r_{\text{S(-II)}} = -\frac{d([\text{S}(-\text{II})])}{dt} = -k_1[S(-\text{II})]^{a_1}[\text{Fe(II)}]^{b_1} \quad (4)
\]

where \( r_{\text{S(-II)}} \) (μM S s\textsuperscript{-1}) is the sulfide precipitation rate. [S(-II)] (μM S) is dissolved sulfide and [Fe(II)] (μM Fe) is iron. \( t \) (sec) is time, \( k_1 \) (μM S\textsuperscript{(1-(a_1+b_1))} s\textsuperscript{-1}) the reaction rate constant and \( a_1 \) (−) and \( b_1 \) (−) are reaction orders with respect to sulfide and Fe(II), respectively.

For precipitation of sulfides with Fe(III), the rate equation (Equation (5)) is basically an extension of Equation (4), as it consists of an initial oxidation step of sulfide to elemental sulfur according to Equation (2).

\[
r_{\text{S(-II)}} = -\frac{d([\text{S}(-\text{II})])}{dt} = -k_2[S(-\text{II})]^{a_2}[\text{Fe(III)}]^{\gamma} - k_1[S(-\text{II})]^{a_1}[\text{Fe(II)}]^{b_1} \quad (5)
\]

where \( k_2 \) (μM S\textsuperscript{(1-(a_2+b_2))} s\textsuperscript{-1}) is the reaction rate constant for the first step of sulfide precipitation using Fe(III) and \( \gamma \) (−) the reaction order with respect to Fe(III).

For reaction times where off-line analysis is not an option, and the products of precipitation cannot be determined, sulfide precipitation must consequently be described in general terms (Equation (6)). Consequently, the different reaction pathways for sulfide precipitation using ferrous and ferric iron, and the dependencies of iron concentrations must all be contained in an overall rate constant for the precipitation reaction.

\[
r_{\text{S(-II)}} = -\frac{d([\text{S}(-\text{II})])}{dt} = -k_{\text{obs}}[\text{S}(-\text{II})]^{\alpha_{\text{obs}}} \quad (6)
\]

where \( k_{\text{obs}} \) (μM S\textsuperscript{(1-\alpha_{\text{obs}})} s\textsuperscript{-1}) is the observed rate constant and \( \alpha_{\text{obs}} \) (−) is the observed reaction order.

Amorphous FeS (K\textsubscript{sp} 1.437·10\textsuperscript{-17} at 25 °C) is the first iron sulfide species to form during precipitation (Davison 1991). It precipitates readily in aqueous solutions and, despite the low solubility constant, it is in equilibrium with...
measurable levels of sulfide in the presence of the amorphous FeS (Davison 1991). This corresponds to practical observations where dissolved sulfides could not be removed completely, even with iron-to-sulfide ratios above the stoichiometric requirement (ASCE 1989). The total sulfide concentration at equilibrium, \([S(-II)_{\text{end}}]\) (µM S) therefore needs to be considered and Equation (6) can be rewritten as Equation (7).

\[
\begin{align*}
\frac{d([S(-II)])}{dt} &= -k_{\text{obs}}([S(-II)] - [S(-II)_{\text{end}}])^{\alpha_{\text{obs}}} \quad (7)
\end{align*}
\]

The rate equation can be solved analytically (Equation (8)).

\[
\begin{align*}
([S(-II)]_{t=0} - [S(-II)_{\text{end}}])^{(1-\alpha_{\text{obs}})} &= \left(\frac{[S(-II)]_{t=0} - [S(-II)_{\text{end}}]}{2}\right)^{(1-\alpha_{\text{obs}})} - k_{\text{obs}}(1 - \alpha_{\text{obs}})t \quad (8)
\end{align*}
\]

where \([S(-II)]_{t=0}\) is the total sulfide concentration (µM S) at time \(t\) (sec) and \([S(-II)]_{t=0}\) is the initial sulfide concentration (µM S).

Using the software R version 3.3.2 (R Core Team 2016) with R studio version 1.1.383 (RStudio Team 2015), the reaction rate constant, \(k_{\text{obs}}\) and \([S(-II)_{\text{end}}]\) were found by fitting to experimental data. The nonlinear least square function modified to include the Levenberg-Marquardt type fitting algorithm (nlSFM) was used. The reaction order, \(\alpha_{\text{obs}}\), was varied in steps of 0.1 between 1.50–2.50 and the \(\alpha_{\text{obs}}\) resulting in maximum \(\Sigma R^2\) was chosen to derive the experiments were kept within the temperature range between 16–26 °C, \(\theta\) can be considered constant as \(T^\circ 293.15\) does not change considerably, and thus one common \(\theta\) of 1.05 was used for all temperature conversions. This theoretic value corresponds well with Nielsen et al. (2004), who experimentally found a \(\theta\) value of 1.06.

**Model equations**

Varying the ratio_{init} of iron-to-sulfide and the pH of the precipitation reactions yields a matrix of multiple related values of \(k_{\text{obs,20}}\) and \([S(-II)_{\text{end}}]\) specific for each of the iron species ((Fe(II)/Fe(III)); buffered water 25/20; Frejlev 7/8; Svenstrup 5/10; Aalborg 7/11), which all were used for constructing the model equations. Spearman rank correlations between variables in the dataset was explored using the software R, and visualized with the corplot v0.84 package (Wei & Simko 2017). Models to describe the best set of regressors based on treatment, medium (expressed by COD), pH, and ratio_{init}, were found by multiple linear regression analysis in the software R using backward elimination. A p-value of 0.05 was used as threshold for deciding when variables and interactions between variables were found to be significant for the models. RMSE was calculated for the models of \(k_{\text{obs,20}}\) and \([S(-II)_{\text{end}}]\). To make the RMSE values comparable between models, data were normalized using feature scaling.

For comparing sulfide precipitation using ferrous and ferric iron the half-life, \(t_{1/2}\) (sec), is used as a benchmark. This number outlines the time it takes before the sulfide concentration reaches half of the initial value (Equation (10)).

\[
t_{1/2} = \left(\frac{\left[\frac{[S(-II)]_{t=0} - [S(-II)_{\text{end}}]}{2}\right]^{(1-\alpha_{\text{obs}})}}{k_{\text{obs,20}}^{1-\alpha_{\text{obs}}}}\right)^{1/(1-\alpha_{\text{obs}})} \quad \text{for } \alpha_{\text{obs}} > 1 \quad (10)
\]

Variables from the dataset using Fe(II) and Fe(III) for precipitation. \(k_{\text{obs}}\) was subsequently converted to \(k_{\text{obs,20}}\) using the Arrhenius equation which is an empirical description of the temperature dependence of reactions (Equation (9)).

\[
k_{\text{obs,20}} = \frac{k_{\text{obs}}}{\theta^T \cdot 293.15} \quad (9)
\]

where \(T\) is temperature in degrees Kelvin, and \(\theta = \exp\left(E_a/(R \cdot (T - 293.15))\right)\), with \(E_a\) being the activation energy [J mol\(^{-1}\)] of ferrous sulfide formation, suggested by Harmandas & Koutsoukos (1996) to be 40 kJ mol\(^{-1}\), and \(R\) the universal gas constant 8.314 J mol\(^{-1}\) K\(^{-1}\). As all

**RESULTS AND DISCUSSION**

Characteristics of buffered water and the sampled wastewaters used for precipitation with ferrous or ferric iron are shown in Table 1.

The concentration of COD and phosphate in the wastewaters for most of the cases corresponded to what can be characterized as low to medium strength wastewater (Henze & Compe 2008). For the ferrous iron experiments, the wastewater from Aalborg West WWTP was sampled the day after a storm event and thus the COD and phosphate concentrations were lower than for typical low strength wastewater. For the ferric iron experiments, the wastewater
from Svenstrup had soluble COD concentration in the range of high strength wastewater. Additionally, the phosphate concentration of the wastewater sampled at Aalborg West WWTP had a lower content of phosphate compared to typical low strength wastewater.

The buffered water for the ferrous experiments was prepared to have what corresponds to a medium concentration of calcium carbonate alkalinity and phosphate (Henze & Comeau 2008). For the alkalinity, this showed, however, only to be around half the concentration of that of the three wastewaters used in the experiments. The high alkalinity of the wastewaters is probably because groundwater, used for public water supply, is extracted from limestone aquifers (Lenton & Muller 2009). In contrast, the phosphate concentration was lower than what is typical for medium strength wastewater (Henze & Comeau 2008). For the Fe(III) experiments, carbonate alkalinity in the buffered water was adjusted to correspond to the alkalinity of the wastewaters. The phosphate concentration was also mixed so it corresponded approximately to the average concentration found in the wastewaters. To ensure comparability between the Fe(II) and Fe(III) tests, ratio\text{init} of the ferric experiments was corrected for the amount lost to phosphate precipitation. The difference in carbonate concentration is believed not to have influenced the precipitation reaction directly. However, as a drop in pH was observed after addition of the iron salts, precipitation in matrices with lower buffer capacities might not be directly comparable with results obtained in this study.

Parameters \( (k_{\text{obs,20}} \text{ and } S(-\text{II})_{\text{end}}) \) of the sulfide decay function were found by fitting Equation (8) to experimental data with constant reaction orders for the two iron salts. The reaction orders that returned the best fit to data were 2.1 and 1.9 for Fe(II) and Fe(III), respectively. This is in line with a previous study in low ionic strength solution that found the reaction to be second order overall for precipitation of sulfide with Fe(II) (Harmandas & Koutsoukos 1996), and in seawater the reaction was found to be first order with respect to both H\(_2\)S and hydrous Fe(III) oxide, thus overall second order (Yao & Miller 1996). Fitted values of \( k_{\text{obs,20}} \) and \( S(-\text{II})_{\text{end}} \) are shown in Figure 1. The ratios are corrected for the amount lost to phosphate precipitation as discussed for Equation (3).

In Figure 1(a) and 1(c), it can be seen that \( k_{\text{obs,20}} \) increased as pH increased, whereas the trend for \( k_{\text{obs,20}} \) as a function of ratio\text{init} was more ambiguous. Where \( k_{\text{obs,20}} \) increased with increasing ratio\text{init} when using Fe(II), a decrease in \( k_{\text{obs,20}} \) when using Fe(III) was observed. It can furthermore be seen that \( k_{\text{obs,20}} \) for the Fe(III) experiments were around a factor of 10 larger than when using Fe(II).

When Fe(II) sulfate was added to aerobic and anaerobic wastewater, FeS precipitated instantaneously judged by visual inspection. Fe(III) in contrary reacted slowly with sulfides in aerobic wastewater (Nielsen et al. 2007). However, Fe(III) added to anaerobic wastewater containing sulfide in a ratio of 0.38 (mol Fe (mol S(-II)) \(^{-1}\)) exhibited a fast reduction to Fe(II) with a parallel oxidation of sulfides. The formation of FeS from this reaction was observed to continue for a time span of a few hours (Nielsen et al. 2005). This contrasts with the results of this study, where sulfide precipitation with both Fe(II) and Fe(III) depending on pH and ratio\text{init} was run to completion within minutes. However, the concentrations of Fe(III) and S(-II) used in this study was a factor 10 and 2–4 higher, and iron salts

| Table 1 | Average values (standard deviation) of key parameters characterizing the wastewaters sampled for the experiments. Buffered water was prepared in the laboratory and values calculated based on the amount of chemicals added |
| Liquid | Alkalinity before adjusting pH to approx. 7 (meq L \(^{-1}\)) | PO\(_4^3\) (μM) | COD\text{dissolved} (mg L \(^{-1}\)) | COD\text{total} (mg L \(^{-1}\)) |
| Fe(II) experiments | | | | |
| Buffered water | 4.05 | 105 | 0 | 0 |
| Frejlev | 8.63 (0.03) | 59.4 (0.6) | 224 (5.5) | 607 (61.5) |
| Svenstrup | 9.62 (0.06) | 75.1 (1.1) | 260 (1.5) | 563 (1.0) |
| Aalborg West WWTP | 8.45 (0.02) | 33.2 (1.4) | 63 (0.1) | 194 (3.8) |
| Fe(III) experiments | | | | |
| Buffered water | 13.5 | 63 | 0 | 0 |
| Frejlev | 13.1 (0.05) | 70.2 (0.2) | 360 (2.5) | 445.6 (6.7) |
| Svenstrup | 13.4 (0.09) | 88.6 (3.0) | 422.5 (8.0) | 499.5 (14.3) |
| Aalborg West WWTP | 11.5 (0.03) | 38.5 (0.8) | 192.5 (5.4) | 213 (7.0) |
were in excess. But, as observed in this study, for Fe(II) a
decrease in ratioinit results in a lower reaction rate constant.

At a comparable Fe(III) concentration but with 20 times
lower sulfide concentration, the rate constant for the oxi-
dation of H2S in seawater with hydrous Fe(III) oxides at
pH of 6–8, S = 56, and 25 °C attained 1.48 × 10^2–4.9 ×
10^2 M^-1 min^-1 (Yao & Miller 1996). Rounding the reaction
orders of 2.1 and 1.9 used in this study to second order,
these rate constants are comparable to and up to a factor
of 1,000 slower than what is observed in this study, depend-
ing on the iron salt used, medium, pH, and ratioinit. A part
of this difference between the rate constants might be
explained by the difference in ionic strength, where an
increase in ionic strength would likely decrease the rate
constant, and furthermore that the sulfide concentration
used was markedly lower (Yao & Miller 1996).

Dependencies of pH on sulfide oxidation rate has pre-
viously been observed. At sulfide concentration <10^-3 M,
the rate of precipitation in buffered water is greater in neu-
tral to acidic conditions for Fe(II) (Rickard 1995). The rate
constant in seawater showed a maximum at pH 6.5, which
is argued to be due to the chemical speciation of H2S and
changes in surfaces sites on the hydrous Fe(III) oxides
used for precipitation (Yao & Miller 1996). However, Fe(III)
added to anaerobic wastewater has been shown to be
quickly reduced to Fe(II) (Nielsen et al. 2005), which could
be an explanation of the fact that in this study k_{obs,20} was
observed to increase with increasing pH.

Figure 1 | Parameters derived from fitting to raw data (points) and model fits of parameters as obtained by multiple linear regression (surfaces) from the Fe(II) and Fe(III) experiments as a function of pH and ratio_{init}. (a) Fe(II) k_{obs,20}, (b) Fe(II) S(-II)_{end}, (c) Fe(III) k_{obs,20}, and (d) Fe(III) S(-II)_{end}. 

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For both Fe(II) and Fe(III), S(-II)$_{\text{end}}$ increased with decreasing pH (Figure 1(b) and 1(d)), which is in line with findings made by Nielsen et al. (2008), but the ratio in that study was below stoichiometric requirements with 0.5 mol Fe(II) (mol S(-II))$^{-1}$. The trend of an increasing S(-II)$_{\text{end}}$ was observed for a decreasing ratio$_{\text{init}}$ when using Fe(II), whereas S(-II)$_{\text{end}}$ for Fe(III) appears to have been unaffected by ratio$_{\text{init}}$ or to only have a slight increasing trend. S(-II)$_{\text{end}}$ attained lower concentrations using Fe(III) compared to using Fe(II). In wastewater at pH 8.3 and a redox potential of 80 mV, the influence of Fe(II) to S(-II)$_{\text{ratio}}$ was investigated. Under these conditions, the fraction of S(-II) precipitated increased with an increasing ratio, but it never attained a fraction of 1, even though Fe(II) was added above the stoichiometric ratio required for FeS formation (Nielsen et al. 2008). This is in line with findings of this study and a study done by Nielsen et al. (2007), where it was observed that only a fraction of the added Fe(II) reacted with dissolved sulfide. An almost equal effectiveness of sulfide precipitation was demonstrated for Fe(II) and Fe(III) at pH 7.6, with ratios ranging from 2.4–6 (mol Fe (mol S(-II))$^{-1}$. At a ratio of 2.4, a removal of around 88% of sulfide by both iron salts was experienced, whereas at higher ratios complete removal took place (Tomar & Abdullah 1994).

Values of $k_{\text{obs,20}}$ and S(-II)$_{\text{end}}$ obtained by fitting to experimental data were modelled by multiple linear regression to yield coefficients for the independent variables of the reactions (surface plots Figure 1(a)–1(d)). To obtain normal distributed residuals between observed and dependent variables, the dependent variables were transformed by natural logarithm before fitting the regression models. In some cases, S(-II)$_{\text{end}}$ became negative. As this was an artefact of the fitting process, an arbitrary constant of 10 was added to all the fitted values prior to ln-transformation of S(-II)$_{\text{end}}$.

Statistical analysis of the dataset revealed that, for $k_{\text{obs,20}}$ of the Fe(II) experiments, there was no significant difference ($p > 0.05$) between buffered water and the three wastewaters. When using Fe(III), the intercept of the regression slope for $k_{\text{obs,20}}$ varied according to the matrix. For a group consisting of the wastewater from Frejlev and Svenstrup, this difference in slope gave rise to a $k_{\text{obs,20}}$ that was 17% of the reaction rate constant for buffered water. Data obtained from sulfide precipitation in wastewater from Aalborg exhibited a 50% reduction in the reaction rate constant compared to buffered water. This suggests that there might be an effect from the matrix, most likely due to the difference in COD concentrations. This was confirmed by a correlation analysis, which showed that $k_{\text{obs,20}}$ had a statistically significant negative correlation with COD for the matrices of Fe(III). In the Frejlev and Svenstrup wastewaters, COD was approximately double the concentration of COD measured for wastewater from Aalborg. As discussed in Nielsen et al. (2005), specific complexing agents present in the wastewater can lower the reactivity of the added iron. Furthermore, Fe(III) is a known coagulant which is used to precipitate organics in, for example, wastewater treatment (Metcalfe & Eddy 2003). These effects could possibly have consumed some of the added Fe(III), which then would make it unavailable for sulfide precipitation, and hence ratio$_{\text{init}}$ would, in principle, be lower in these cases.

Grouping all media for the Fe(III) dataset and constructing one common model reveals that the resultant $k_{\text{obs,20}}$ would be around 50% of $k_{\text{obs,20}}$ as modelled for buffered water alone. This corresponds to a $k_{\text{obs,20}}$ equal to the wastewater of Aalborg, but is still higher than the wastewaters of Frejlev and Svenstrup.

Regression analysis suggested that wastewater from Frejlev and Svenstrup should have individual models of S(-II)$_{\text{end}}$ for Fe(II) and Fe(III), respectively. However, these two models exhibited a reversed trend compared to the models of the remaining groups of media. Scrutinizing the dataset for these series suggests that a single outlier in the datasets explained this effect. Furthermore, a correlation analysis did not show any significant interaction between S(-II)$_{\text{end}}$ and COD of the matrices of either Fe(II) or Fe(III). It was hence decided to build the regression models, irrespective of the medium used for sulfide precipitation. Coefficients for intercept, pH, and ratio$_{\text{init}}$ used to describe ln($k_{\text{obs,20}}$) ($R^2 = 0.81$) and ln(S(-II)$_{\text{end}}$ + 10) ($R^2 = 0.35$) for each specific treatment were derived from multiple linear regression. A back-transformation of the obtained regression models then yields equations describing $k_{\text{obs,20}}$ and S(-II)$_{\text{end}}$ for precipitation with Fe(II) (Equations (11) and (12)) and Fe(III) (Equations (13) and (14)). As described earlier, an arbitrary constant of 10 was added to the parameter S(-II)$_{\text{end}}$ to perform ln-transformation of the dataset before multiple linear regression. Upon backward transformation, this constant must consequently be subtracted again as done in Equations (12) and (14).

\[ k_{\text{obs,20,Fe(II)}} = e^{(-12.64 + 0.25pH - 8.75\text{Ratio}_{\text{init}} + 1.35pH \text{Ratio}_{\text{init}})} \]  \hspace{1cm} (11)

\[ S(-II)_{\text{end,Fe(II)}} = e^{(7.78 - 0.42pH - 1.05\text{Ratio}_{\text{init}})} - 10 \]  \hspace{1cm} (12)

\[ k_{\text{obs,20,Fe(III)}} = e^{(-25.98 + 2.59pH + 4.03\text{Ratio}_{\text{init}} - 0.53pH \text{Ratio}_{\text{init}})} \]  \hspace{1cm} (13)

\[ S(-II)_{\text{end,Fe(III)}} = e^{(5.22 - 0.42pH + 0.05\text{Ratio}_{\text{init}})} - 10 \]  \hspace{1cm} (14)
RMSE between calculated values of \( k_{\text{obs},20} \) and \( S(-\text{II})_{\text{end}} \) obtained from the regression models and the measured data were 0.09 and 0.18 for Fe(II) and for Fe(III) 0.20 and 0.14, respectively. Generally, the model equations described \( k_{\text{obs},20} \) and \( S(-\text{II})_{\text{end}} \) derived from the raw data with good approximation for most of the pH conditions and iron-to-sulfide ratios as can be seen in Figure 1(a)–1(d). However, at low \( \text{ratio}_{\text{init}} \) for Fe(II), it seems that the model tends to underestimate the residual sulfide concentration. Whereas an underestimation of \( k_{20,\text{obs}} \) for Fe(III) seems to be the outcome of the model at a low \( \text{ratio}_{\text{init}} \) and a high pH value.

Within the bounds of pH and \( \text{ratio}_{\text{init}} \) used to derive Equations (11)–(14), the output from these equations can be used to calculate the time it will take to reach half initial sulfide concentration \( (t_{\text{1/2}}) \) (Equation (10)). In Figure 2, this is done for a dissolved sulfide concentration of 300 \( \mu \text{M} \) as being representative of wastewater with a high sulfide concentration (Hvitved-Jacobsen et al. 2013).

From Figure 2, it can be seen that the time to reach half of initial sulfide concentration at low pH and low \( \text{ratio}_{\text{init}} \) is considerably faster using Fe(III) than when using Fe(II). Increasing pH together with \( \text{ratio}_{\text{init}} \) decreases \( t_{\text{1/2}} \) for both iron salts. From the correlation patterns of \( k_{\text{obs},20} \) and \( S(-\text{II})_{\text{end}} \) with pH and \( \text{ratio}_{\text{init}} \) (Figure 3), it can be seen in Figure 3(a) that \( k_{\text{obs},20} \) for Fe(II) exhibits a statistically significant positive correlation with both pH and \( \text{ratio}_{\text{init}} \). Fe(III), on the other hand, does not show a significant correlation between \( k_{\text{obs},20} \) and \( \text{ratio}_{\text{init}} \), but only a significant positive correlation with pH (Figure 3(b)).

For \( S(-\text{II})_{\text{end}} \), Fe(III) yields a constant low concentration (Figure 1(d)), which is only marginally affected by pH. Even though only marginally affected, the correlation between these two parameters is statistically significant, whereas \( \text{ratio}_{\text{init}} \) is statistically uncorrelated herewith. In contrast, hereto, a large \( S(-\text{II})_{\text{end}} \) must be expected when using Fe(II) under conditions of low pH and low \( \text{ratio}_{\text{init}} \). As \( S(-\text{II})_{\text{end}} \) is negatively correlated with both parameters (Figure 3(a)), an increase of these will consequently decrease \( S(-\text{II})_{\text{end}} \). The decrease in effectiveness of sulfide
precipitation observed at low pH is in line with Boon (1995),
who states that the effect of iron salts below pH 6.5 would be poor. The reason that Fe(III) yields good precipitation efficiency over the whole pH range, might be a combination of an additional 0.5 mol S (mol Fe(III))\(^{-1}\) being removed by oxidation to elemental sulfur during the reduction of Fe(III) to Fe(II) (Equation (2)) and that the presence of elemental sulfur might enhance formation of pyrite from amorphous ferrous sulfide. As pyrite is less soluble than amorphous ferrous sulfide, this will shift the equilibrium and hence maintain S(-II)\(_{end}\) low (Rickard & Luther 2007).

Findings of the present study are applicable for the water industry when designing sulfide abatement solutions or when using conceptual sewer process models for planning sulfide abatement strategies. In cases where end-of-pipe abatement is to be applied, knowledge about reaction kinetics is essential. Based on this work, the required reaction times can be calculated to achieve proper abatement before discharge of sewage from a force main. This study furthermore shows that, when applying Fe(II) for sulfide abatement, both the amount of iron added and the pH is of significant importance, whereas for Fe(III) it is only pH that influences kinetics.

**CONCLUSIONS**

Sulfide precipitation rates were demonstrated to be faster using Fe(III) compared to using Fe(II) under anaerobic conditions when sulfide was present in the matrix before the addition of the iron salts. It furthermore showed that, for Fe(II), there was no statistically significant effect of the matrix on the rate constants. For Fe(III), an effect of the matrix was observed, most likely caused by the difference in COD. However, the specific compounds responsible for this observation were not determined.

Rate equations for sulfide precipitation using Fe(II) and Fe(III) in wastewater were established with observed rate orders of 2.1 and 1.9, respectively. For both iron salts, precipitation rates increased with increasing pH. The lack of correlation between \(k_{obs,20}\) and S(-II)\(_{end}\) with \(\text{ratio}_{init}\) for Fe(III) implies that sulfide control should be performed solely by adjusting pH while keeping \(\text{ratio}_{init}\) close to stoichiometric requirements. For Fe(II), on the other hand, an increase in \(\text{ratio}_{init}\) increased precipitation rates, and pH as well as \(\text{ratio}_{init}\) should therefore be increased to obtain proper sulfide control.

Model equations, based on experimental data, are proposed to predict rate constants \(k_{obs,20}\) and concentrations of sulfide left at equilibrium conditions \(S(-\text{II})_{end}\), within the range of iron-to-sulfide ratios and pH used in this study. These values can then be applied in Equation (10) to predict reaction times needed for proper sulfide control in end-of-pipe abatement applications of sewer force mains.

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