Chemical sulfide oxidation of wastewater – effects of pH and temperature

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Abstract In this study, the kinetics and stoichiometry of chemical sulfide oxidation of wastewater from sewer networks were investigated. Based on experiments, it was shown that the stoichiometry could be considered identical for wastewater from two sampling sites. However, the kinetics differed significantly among the wastewaters from the two sites. Effects of pH and temperature were investigated in the pH and temperature ranges 5–9 and 5–25°C, respectively. The rate of chemical sulfide oxidation could be related to the dissociation of $H_2S$ to HS$^-$, with HS$^-$ being oxidized at a higher rate than $H_2S$. The temperature dependency of the chemical sulfide oxidation rate was described using an Arrhenius relationship. The oxidation rate was found to double with a temperature increase of 12°C. The stoichiometry of the chemical oxidation was not significantly affected by varying pH and temperature. Based on the experiments, a general rate equation, including a stoichiometric coefficient describing chemical sulfide oxidation in wastewater was proposed, enabling the process to be incorporated into sewer process models that can predict odor and corrosion problems.

Keywords Corrosion; hydrogen sulfide; odor; oxidation; rate equation; sewer networks

Introduction

The occurrence of sulfide caused by septicity of wastewater in sewer networks is a common phenomenon, which is associated with an array of potential problems such as odor, concrete and metal corrosion, and health-related aspects. Sulfide in wastewater is primarily produced by anaerobic respiration taking place within the biofilm and sediment covering the submerged sewer walls. From the biofilm and sediment, the sulfide diffuses into the flowing wastewater, where it will react by one of several possible reactions:

- Emission into the sewer atmosphere as hydrogen sulfide gas, potentially resulting in corrosion and odor problems.
- Chemical or biological oxidation by dissolved oxygen (DO), which transforms the sulfide to sulfate or various intermediates.
- Reaction with metal ions, which results in formation of insoluble metal sulfides.

As sulfide in sewer networks is produced together with other odorous compounds, including low-molecular-weight fatty acids and volatile sulfur and nitrogen compounds, it may be an effective indicator for odor problems. Thistlethwayte and Goleb (1972) stated that although the hydrogen sulfide concentration alone may not be a sufficient measure of potential sewer air odor levels, hydrogen sulfide concentration measurements probably are sufficient for most studies of sewer gases.

Several empirical models have been developed to predict potential sulfide levels in pressure mains and gravity sewers. Such models have been used for both sewer design and managing sulfide formation and its effects (Hvitved-Jacobsen and Nielsen, 2000). However, these empirical models do not account for all the major factors affecting the occurrence of sulfide in sewer networks and the effects in terms of odor and corrosion. Therefore, development of new reliable model concepts to predict occurrence of sulfide in sewer networks is needed.
In this study, the kinetics and stoichiometry of chemical sulfide oxidation in wastewater as a function of pH and temperature were investigated. Based on a series of experiments, a general rate equation and stoichiometric coefficient enabling chemical sulfide oxidation to be included in sewer process models, are proposed.

Methods

Sampling and sample preparation
Wastewater was collected from two sites: Frejlev Sewer Research and Monitoring Station, Denmark, and Aalborg East wastewater treatment plant (WWTP), Denmark. Sampling was conducted in the period from March 2002 to February 2003. The upstream catchment area of the sampling site in Frejlev serves approximately 2,000 person equivalents, and is without significant industries. The residence time of wastewater in the catchment of Frejlev is small, and most of the sewer pipes are laid with steep slopes, thus, the wastewater is aerobic throughout most of the system. Aalborg East WWTP serves approximately 70,000 person equivalents, and receives wastewater from both residential and industrial areas. The catchment of Aalborg East WWTP is extensive and includes several pressure mains. This wastewater is therefore subject to both aerobic and anaerobic conditions.

In Frejlev, samples were collected directly from the sewer pipe. At Aalborg East WWTP, the samples were collected at the inlet to the treatment plant. Immediately after sampling, the wastewater was brought back to the laboratory and autoclaved in order to inhibit all biological activity, thereby preventing any biological sulfide oxidation in the experiments. Autoclaving was usually initiated within one hour of sampling.

Measurement of sulfide oxidation kinetics
The kinetics and stoichiometry of chemical sulfide oxidation in wastewater were measured using a batch reactor set-up operated with pulse dosing of sulfide and DO, according to Nielsen et al. (2003). The batch reactor was operated at sulfide and DO concentrations between 8 and 0 g S m$^{-3}$, and 4 and 0 g O$_2$ m$^{-3}$, respectively. Total sulfide concentration was determined by the methylene blue method and DO concentration was measured using a PreSens Microx TX2 fiber optic oxygen micro-sensor. Experiments were conducted on wastewater that had settled for 15 minutes, thereby preventing particulates from clogging equipment for collecting samples for sulfide analysis. Figures 1a and 1b show sulfide and DO concentration versus time during an experiment. Figures 1c and 1d show the corresponding removal rates of total sulfide and DO, and a model describing the kinetics. The effects of temperature were investigated at temperatures between 5°C and 25°C at pH 8.0. Experiments on the effects of pH were conducted at pH between 5.0 and 9.0 at 20°C. Other experiments were conducted at pH 8.0 and 20°C. The wastewater was buffered using TRIS buffer (NH$_2$C(CH$_2$OH)$_3$) at pH 9.0 and 8.0, MES buffer (C$_6$H$_{13}$NO$_4$S) at pH 7.0 and 6.0, and acetate buffer (CH$_3$COOH) at pH 5.0. The buffer concentrations were 0.005 M and all buffers were PA grade. The effect of buffers on the sulfide oxidation rate was tested and found not to affect the results at the concentrations employed.

Figure 1 Concentrations and removal rates of total sulfide and DO during an experiment, cf. text
For assessment of general chemical sulfide oxidation kinetics, and temperature and pH effects, three different types of experiments were conducted (Table 1).

1. Experiments conducted on single independent samples at constant experimental conditions.
2. Triplicate experiments in which one wastewater sample of 15 liters was divided into three 5-liter subsamples. Independent experiments on each of the three subsamples were then conducted at different experimental conditions.
3. Experiments on single samples in which pH was maintained constant at different values in a sequence of periods. Typically, the experiments were conducted at five different pH values each maintained for a period of 1–2 hours. In such experiments, no buffer was added, and accordingly the pH changed slightly at each pH value during the experiment.

The effects of temperature were investigated using wastewater from Frejlev only, whereas the effects of pH were investigated using wastewater from both Frejlev and Aalborg East.

**Rate equation and stoichiometry**

At constant pH, ionic strength and temperature, the kinetics of chemical sulfide oxidation can be described by a rate equation of the form (Chen and Morris, 1972a):

\[
\frac{d[S(-II)]}{dt} = k[S(-II)]^\alpha[DO]^\beta
\]

where \( k \) is sulfide oxidation rate [\( g \text{ S m}^{-3} \text{ h}^{-1} \)]; \( S(-II) \) is total sulfide, i.e. \( H_2S + HS^- + S^{2-} \) [\( g \text{ S m}^{-3} \)]; \( DO \) is dissolved oxygen [\( g \text{ O}_2 \text{ m}^{-3} \)]; \( k \) is the reaction rate constant \( [(g \text{ S m}^{-3})^{-\alpha}(g \text{ O}_2 \text{ m}^{-3})^{-\beta}\text{h}^{-1}] \); \( \alpha \) is the reaction order with respect to total sulfide [–] and \( \beta \) is the reaction order with respect to DO [–].

The kinetic parameters were determined by model calibration, i.e. by repeated simulation of experimental results until the best agreement between simulated and measured concentrations was achieved. The agreement between simulated and measured sulfide concentrations was optimized by least-squares analysis. Simulation of the measurements was performed using the Euler method.

The stoichiometry of chemical sulfide oxidation was determined in terms of the reaction coefficient, \( R_{C,chem} \), as defined by Cline and Richards (1969).

\[
R_{C,chem} = \frac{a}{b}
\]

where \( a \) and \( b \) are stoichiometric coefficients, i.e. \( a S(-II) + b O_2 \rightarrow \text{Products} \) [\( \text{mol S} \)] or [\( \text{mol O}_2 \)].

\( R_{C,chem} \) was explicitly found as the slope of total sulfide versus DO concentrations in the sulfide oxidation experiments, according to Nielsen et al. (2003).

**Effects of temperature and pH**

The effect of temperature on oxidation kinetics was interpreted in terms of an Arrhenius relationship. Integration of the Arrhenius equation between temperatures \( T_1 \) and \( T_2 \) within a

<table>
<thead>
<tr>
<th>Wastewater</th>
<th>pH 8, 20°C</th>
<th>Temperature effects</th>
<th>pH effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frejlev</td>
<td>1</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Aalborg East</td>
<td>1</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>

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A. Haaning Nielsen et al. 187
narrow temperature interval is approximated by Eq. (3) (Hvitved-Jacobsen, 2002). In Eq. (3), \( \theta \) is referred to as the Arrhenius constant.

\[
\left( \frac{d[S(-II)]}{dr} \right)_{T_2} = \left( \frac{d[S(-II)]}{dr} \right)_{T_1} \theta^{(T_2-T_1)} \tag{3}
\]

The effect of pH on the sulfide oxidation rate can be related to differences in reactivity between oxygen and different sulfide species, as shown in Eqs (4) and (5) (Millero et al., 1987).

\[
\begin{align*}
H_2S + O_2 & \stackrel{k_0}{\longrightarrow} \text{products} \tag{4} \\
HS^- + O_2 & \stackrel{k_1}{\longrightarrow} \text{products} \tag{5}
\end{align*}
\]

where \( k_0 \) is the rate constant for oxidation of \( H_2S \) and \( k_1 \) is the rate constant for oxidation of \( HS^- \). Accordingly, at varying pH, the rate of sulfide oxidation can be described by Eq. (6) (Millero et al., 1987).

\[
\left( -\frac{d[S(-II)]}{dr} \right)_{[H^+]} = \frac{k_0 + k_1K_1/[H^+]}{1 + K_1/[H^+]} [S(-II)]^\alpha [O_2]^\beta
\]

In Eq. (6), \( K_1 \) is the first dissociation constant for \( H_2S \) (\( \approx 1.0 \times 10^{-7} \)).

The parameters \( \theta, k_0 \) and \( k_1 \) in Eqs (3) and (6) were determined by the least-squares method.

**Results and discussion**

**Oxidation kinetics at constant pH and temperature**

Multiple experiments on chemical sulfide oxidation at pH 8, 20°C, were conducted. Using wastewater from Frejlev and Aalborg East, 24 and 11 experiments were conducted, respectively. The distributions of kinetic parameters determined from simulation of experimental results are shown in Figure 2. The Lilliefors test showed that all parameters could be considered to be log-normally distributed (\( P > 0.2 \)), although normal distribution showed better agreement with the rate constant, \( k \), in wastewater from Frejlev. Correlation analysis of the kinetic parameters showed that the rate constant, \( k \), and the reaction order with respect to sulfide, \( \alpha \), were correlated with a correlation coefficient of –0.79 in experiments on wastewater from Frejlev, i.e. high values of \( k \) corresponded to low values of \( \alpha \). No other correlation among the parameters was statistically significant at a 5% level of significance. The mean value and 95% confidence limits of the kinetic parameters determined from simulation of chemical sulfide oxidation experiments are listed in Table 2.

![Figure 2](https://iwaponline.com/wst/article-pdf/50/4/185/421703/185.pdf)

**Figure 2** Log-normal probability plots of kinetic parameters for chemical sulfide oxidation in wastewater, and log-normal distributions calculated from the sample means and standard deviations.
Mean values and confidence limits are calculated from log-transformed data, and the results retransformed to linear scale. The average reaction rate constant was significantly higher in the wastewater from Aalborg East ($P < 0.01$). Literature values on reaction rate constants of chemical sulfide oxidation in wastewater are almost non-existent. A comparison with rate constants from studies on other matrices is not relevant, as the kinetics of chemical sulfide oxidation in wastewater are in general much faster than in clean water. This is presumably owing to catalysis of the reaction by wastewater constituents. Chen and Morris (1972b) found several organic compounds, some of which are abundantly found in wastewater, to significantly increase the rate of chemical sulfide oxidation. Wilmot et al. (1988) determined the kinetic parameters for the mixed chemical and biological sulfide oxidation in active wastewater in which the biological sulfide oxidation on average was found to account for less than 40% of the total oxidation. In their study, the rate constant was not assessed in terms of a power function; nevertheless, reaction orders with respect to each reactant were determined. They presented data showing sulfide oxidation rates of the same order of magnitude as can be calculated using the reaction rate constants given in Table 2. The reaction rate constant is characterized by a smaller confidence interval for the wastewater from the small well-defined catchment of Frejlev compared to rate constants for the wastewater from the extensive Aalborg East catchment.

In experiments on wastewater from Frejlev, the overall reaction order is approximately 1 while oxidation kinetics in the wastewater from Aalborg East are described by a rate equation of slightly higher order, approximately 1.2. The reaction order with respect to each reactant was of similar magnitude in wastewater from both Frejlev and Aalborg East. The reaction orders are in good agreement with findings by Wilmot et al. (1988) of reaction orders in the interval 0.6–1.2 for total sulfide, and of approximately 0.2 for DO in experiments using active wastewater. Literature values on the kinetics of chemical oxidation in buffered water and seawater differ significantly from those reported for wastewater, in that the overall reaction order has been shown to be approximately 2. Chen and Morris (1972a) found the overall reaction order to be 1.9, with the order being 1.34 and 0.56 with respect to total sulfide and DO, respectively. Birkner and O’Brien (1977) found the reaction order to be 1.02 for total sulfide and 0.80 for DO. Cline and Richards (1969) and Millero et al. (1987) simulated their data with a rate equation where the reaction order was 1 in each reactant. Conversely, Buisman et al. (1990) reported the reaction order to be 0.597 and 0.642 with respect to total sulfide and DO, respectively.

Stoichiometry of chemical sulfide oxidation

The stoichiometry was investigated in all experiments. Normal probability plots of reaction coefficients determined at pH 8, 20°C, using wastewater from both Frejlev and Aalborg East, are shown in Figure 3.

The normal probability plots show that the reaction coefficients are normally distributed and are of similar magnitude for wastewater from the two sampling sites. Experimentally determined reaction coefficients in wastewater from Frejlev and Aalborg East are shown in Table 3. The stoichiometry of chemical sulfide oxidation is complex, because of a wide

| Table 2 Parameters for chemical sulfide oxidation in wastewater from Frejlev and the inlet to Aalborg East WWTP at pH 8.0, 20°C. Mean values (95% confidence limits) of kinetic parameters are given |
|---|---|---|---|
| Parameter | $n$ | $k$ | $\alpha$ | $\beta$ |
| | | [$(gS m^{-3})^{n-1} (gO_2 m^{-3})^\alpha (h^{-1})^\beta$] | [\$] | [\$] |
| Frejlev catchment | 24 | 0.24 (0.22; 0.27) | 0.81 (0.76; 0.86) | 0.19 (0.15; 0.22) |
| Inlet to Aalborg East WWTP | 11 | 0.46 (0.33; 0.65) | 0.99 (0.88; 1.12) | 0.18 (0.12; 0.27) |
array of products and intermediates produced during the course of the reaction. However, the most commonly observed species are thiosulfate (S$_{2}$O$_{3}^{2–}$), sulfite (SO$_{3}^{2–}$) and sulfate (SO$_{4}^{2–}$) (Birkner and O’Brien, 1977). Based on this, a reaction coefficient between 0.5 gS (g O$_{2}$)$^{-1}$ and 1.0 gS (g O$_{2}$)$^{-1}$ is expected. This value agrees well with the experimentally determined values (Figure 3 and Table 3). As shown by Nielsen et al. (2003) the reaction coefficient can be considered constant during the course of the reaction, i.e. further oxidation of intermediates to sulfate proceeds at a slow rate compared to the rate of sulfide oxidation.

Effects of pH and temperature

Figure 4 shows the effects of pH and temperature on the kinetics of chemical sulfide oxidation in wastewater. The effects are assessed by an apparent rate constant, $k^*$, determined by simulating the experiments using Eq. (1) with values of $\alpha$ and $\beta$ of 0.9 and 0.2, respectively.

The effect of changing the temperature on the kinetics was successfully described by the Arrhenius equation (Figure 4a). From the three independent experiments, the Arrhenius constant, $\theta$, was determined at 1.06 with a standard deviation of 0.01, corresponding to a doubling of the rate with a temperature increase of 12°C. This is in reasonable agreement with the finding by Wilmot et al. (1988) that the rate of sulfide oxidation in active wastewater approximately doubles over a 15°C temperature increase. For the chemical oxidation of sulfide in water and seawater, the energy of activation has been reported in the range of 33.5–47 kJ mol$^{-1}$, corresponding to a doubling in the rate with a temperature increase of approximately 14–10°C (Avrahami and Golding, 1968; Millero et al., 1987). No temperature effects on the reaction order with respect to each reactant or on the stoichiometry of chemical sulfide oxidation were found in the investigated temperature interval.

The effect of pH on the sulfide oxidation rate was found to represent the dissociation of H$_{2}$S to HS$^-$ with HS$^-$ being oxidized at a higher rate than H$_{2}$S, although, the results were somewhat scattered (Figure 4b). In addition, the rate in each sample was subject to significant variability. Some samples were characterized by a potential for high rate chemical sulfide oxidation at all pH values investigated, whereas the reaction was apparently slower
in other samples. For this reason, two sets of parameters describing 90% of the variation are
proposed. The parameters were determined by manually changing the values of \( k_0 \) and \( k_1 \) in
Eq. (6) until >90% of the measured rates were within the interval predicted by the two
parameter sets as indicated by the dashed lines in Figure 4b. The kinetic parameters are
given in Table 4.

Wastewater from Aalborg East exhibited chemical sulfide oxidation rates in the entire
range of \( k_0 \) and \( k_1 \). In wastewater from Frejlev, \( k_0 \) also exhibited large variability whereas \( k_1 \)
appeared to be in best agreement with the low-rate value. The results are consistent with
findings by Millero et al. (1987) who found the same type of pH dependency for sulfide
oxidation in seawater. For the oxidation of sulfide by peroxide, Hoffmann (1977) found
similar characteristics in the pH range 3–8.

Linear regression analysis showed that the stoichiometry was also affected by varying
pH. The reaction coefficient decreased with increasing pH from 0.98 (\( n = 7 \)) at pH 6 to 0.72
(\( n = 7 \)) at pH 9. However, the change in stoichiometry was not statistically significant at a
2.5% level. As a simplification, the reaction coefficient can therefore be considered con-
stant for modeling purposes. The finding that an increase in pH resulted in more oxidized
products disagrees with product formation reported by Birkner and O’Brien (1977) who
found sulfate to be the favored reaction product at pH below 6, and sulfite, thiosulfate and
sulfate to be the significant products at pH above 7. The reason for this discrepancy is not
yet clear. The effects of ionic strength were not investigated, as the natural variation in ionic
strength of wastewater is negligible compared with reported kinetic effects of varying ionic
strength (Nielsen et al., 2003).

**General rate equation and stoichiometry**

Based on the entire range of experiments and taking into consideration the variability of the
kinetic parameters, a general rate equation is proposed (Eq. (7)).

\[
r_{\text{S(-II),Oxidation}} = \frac{k_0 + k_1 K_1 / [H^+]}{1 + K_1 / [H^+] [S(-II)]^{0.9} [O_2]^{0.2} 1.06^T^{-20}}
\]

**Table 4** Kinetic parameters for the chemical oxidation of \( \text{H}_2\text{~S} (k_0) \) and \( \text{HS}^- (k_1) \) in wastewaters from Frejlev
and Aalborg East

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Low rate</th>
<th>High rate</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_0 ) ((\text{gS m}^{-3})^{0.1} (\text{gO}_2\text{ m}^{-3})^{-0.2} \text{ h}^{-1})</td>
<td>0.02</td>
<td>0.08</td>
<td>0.04*</td>
</tr>
<tr>
<td>( k_1 ) ((\text{gS m}^{-3})^{0.1} (\text{gO}_2\text{ m}^{-3})^{-0.2} \text{ h}^{-1})</td>
<td>0.25</td>
<td>1.00</td>
<td>0.50*</td>
</tr>
</tbody>
</table>

* both \( k_0 \) and \( k_1 \) were found to be log-normally distributed
$k_0$ and $k_1$ are subject to significant variability and should therefore be employed with caution. As a conservative estimate in the prediction of sulfide build-up, the set of low-rate parameters given in Table 4 may be used. For the typical situation, a set of average parameters is proposed (Table 4). The rate equation is valid within the pH and temperature intervals of 6–9 and 5°C–25°C, respectively. The corresponding reaction coefficient, $R_{C,Chem}$, is recommended at a value of 0.8 gS (g O$_2$)$^{-1}$.

Conclusions

The kinetics and stoichiometry of chemical sulfide oxidation in wastewater from sewer networks were investigated. The effects of pH were demonstrated to represent the dissociation of H$_2$S, with HS$^-$ being more readily oxidized than H$_2$S. The effects of changing temperature were successfully described by an Arrhenius dependency. A general rate equation and stoichiometric coefficient describing chemical sulfide oxidation at varying pH and temperature conditions was proposed. This enables the process to be included in sewer process models, thus improving their capability to predict the occurrence of sulfide and thereby odor nuisance.

References


