

Determination of Kinetics and Stoichiometry of Chemical Sulfide Oxidation in Wastewater of Sewer Networks

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A method for determination of kinetics and stoichiometry of chemical sulfide oxidation by dissolved oxygen (DO) in wastewater is presented. The method was particularly developed to investigate chemical sulfide oxidation in wastewater of sewer networks at low DO concentrations. The method is based on continuous measurement of the reactants allowing the kinetics to be determined at varying reactant concentrations during the course of the experiment. The kinetics determined was simulated by a rate equation. The precision of the method was assessed in terms of the standard deviation of the kinetic parameters determined in a triplicate experiment. The kinetic parameters determined in 25 experiments on wastewater samples from a single site exhibited good constancy with a variation of the same order of magnitude as the precision of the method. It was found that the stoichiometry of the reaction could be considered constant during the course of the experiments although intermediates accumulated. This was explained by an apparent slow oxidation rate of the intermediates. The method was capable of determining kinetics and stoichiometry of chemical sulfide oxidation at DO concentrations lower than 1 g of O₂ m⁻³.

Introduction

The occurrence of hydrogen sulfide in the sewer atmosphere is associated with an array of potential problems including malodors and corrosion (1, 2). Sulfide in sewer networks originates primarily from anaerobic sulfate respiration taking place in the anaerobic regions of the biofilm covering the submerged sewer walls and in the sediments. From the anaerobic regions in the biofilm and sediment, the sulfide diffuses toward the bulk water. At high dissolved oxygen (DO) concentrations in the bulk water, some or all of the sulfide will be oxidized within the aerobic regions in the biofilm and sediment. At low DO concentration, however, sulfide may escape into the bulk water. In the absence of DO, all the sulfide produced will enter the bulk water. When present in the bulk water, the sulfide will be oxidized, emitted to the sewer atmosphere, or react with metal ions to form insoluble metal sulfides (2, 3). Sulfide oxidation in the water phase is particularly of importance in gravity sewers.

When addressing sulfide problems in sewer networks, predictive models are highly useful tools. One such model

is the WATS model (Wastewater Aerobic/anaerobic Transformations in Sewers) developed to simulate carbon and sulfur transformations (4). At the present state, sulfur transformations have been included in the model although not fully integrated. The model accounts for formation of sulfide in the biofilm and sediments (sulfate respiration). Emission of sulfide is at present being included (5). However, the major sinks for sulfide in the wastewater itself, including oxidation and precipitation, have not been dealt with. An integration of the entire sulfur cycle in the WATS model implies these processes to be better understood.

This paper presents a method to determine kinetics and stoichiometry of chemical sulfide oxidation by DO in wastewater. The method was developed to study chemical sulfide oxidation at sulfide and DO concentrations resembling in situ conditions, particularly low levels of DO. The method may also be applied for determination of kinetics and stoichiometry of biological sulfide oxidation. In addition, the existing knowledge on sulfide oxidation is discussed in this context.

Background

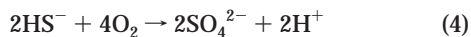
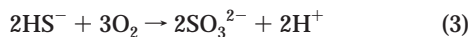
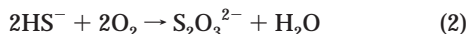
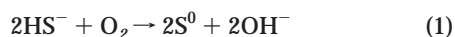
Reaction kinetics and stoichiometry of sulfide oxidation have been studied in various aqueous systems. Most work has dealt with sulfide oxidation in seawater, buffer solutions, and cell suspensions. Only a few studies have focused on sulfide oxidation in wastewater (i.e., most of the understanding of the sulfide oxidation process originates from work on matrixes with different characteristics than wastewater). Compared to seawater and buffer solutions, wastewater is characterized by a high concentration of organic matter, a large active biomass, and a relatively low ionic strength. All these factors are known to exert effects on the oxidation process (6, 7).

Sulfide Oxidation in Wastewater. In wastewater, both chemical and biological sulfide oxidation occurs (6). The literature is inconsistent on the relative importance of chemical and biological oxidation in wastewater. It is, however, likely that both processes are significant. The U.S. EPA (6) stated that the biological oxidation of sulfide proceeds with a higher rate than the chemical oxidation but did not give quantitative information in this respect. From experiments on both active and sterilized wastewater, Wilmot et al. (7) found the biological sulfide oxidation to account for 12–56% of the total oxidation rate. Kotronarou and Hoffmann (8) reported a more pronounced effect of sterilization. They found the oxidation rate in autoclaved wastewater to be approximately 30% of the rate in active wastewater. Jolley and Forster (9) compared the oxidation rate in buffered water to the rate in wastewater and found the rate in buffered water to be the fastest. However, the oxidation rate in buffered water may differ significantly from the chemical oxidation rate in wastewater owing to potential catalysis and inhibition by wastewater constituents.

Reaction Mechanism and Stoichiometry of Chemical Sulfide Oxidation. The chemical sulfide oxidation is believed to be a chain reaction and for that reason very sensitive to reaction conditions (3, 10, 11). Several studies report the reaction to be preceded by an induction period of up to several hours while others do not report on this effect (12). Chen and Morris (13) found some correlation between the length of the induction period and the initial oxidation rate, indicating that the length of the induction period decreases with increasing initial oxidation rate. The stoichiometry of chemical sulfide oxidation is complex because of the various products and intermediates produced during the course of

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the reaction (8). The major intermediates and products identified are elemental sulfur (S^0), thiosulfate ($S_2O_3^{2-}$), sulfite (SO_3^{2-}), and sulfate (SO_4^{2-}). The intermediates and products are formed according to eqs 1–4 (14):



Findings of polysulfides, mainly S_4^{2-} and S_5^{2-} , which originate from a reaction between elemental sulfur and sulfide ions, have been reported (13). In water, further chemical oxidation of thiosulfate and sulfite has been shown to proceed at a significantly lower rate than that of sulfide oxidation (11, 15). Especially, thiosulfate is oxidized very slowly and may therefore be considered a stable reaction product depending on the time scale considered.

Kinetics of Chemical Sulfide Oxidation. At constant pH, ionic strength, and temperature, the kinetics of chemical sulfide oxidation has been described by a rate equation of the general form (13, 15, 16):

$$r_{H_2S, \text{oxidation}} = - \frac{d(S(-II)_T)}{dt} = k[S(-II)_T]^\alpha [DO]^\beta \quad (5)$$

where $S(-II)_T$ is the total sulfide (i.e., $H_2S + HS^- + S^{2-}$) (g of $S \text{ m}^{-3}$); k is the reaction rate constant [(g of $S \text{ m}^{-3}$) $^{1-\alpha}$ (g of $O_2 \text{ m}^{-3}$) $^{-\beta} \text{ h}^{-1}$]; α is the reaction order with respect to total sulfide (-); and β is the reaction order with respect to DO (-).

In the literature, some discrepancy concerning the magnitude of the reaction rate constant of chemical sulfide oxidation exists. Varying experimental conditions preclude a comparison of all the proposed rate equations; however, from experiments conducted under similar conditions, the discrepancy is evident as discussed by a number of authors (12, 16, 17). Generally it is found that, in buffered water at near-neutral pH and air saturation, chemical sulfide oxidation proceeds very slowly with half-times of total sulfide on the order of days. For wastewater, the chemical sulfide oxidation has also been reported to be slow when either reactant is present in concentrations of less than 1 g m^{-3} (3).

For the chemical oxidation in buffered water and seawater, the overall reaction order has been shown to be approximately 2. Chen and Morris (13) found the overall reaction order to be 1.9, with the order being 1.34 and 0.56 with respect to total sulfide and oxygen, respectively. O'Brien and Birkner (15) found the reaction order to be 1.02 for total sulfide and 0.80 for oxygen. Cline and Richards (14) and Millero et al. (17) simulated their data by a kinetic rate equation where the reaction order was 1 in each reactant. Conversely, Buismann et al. (16) reported the reaction order to be 0.597 and 0.642 with respect to total sulfide and oxygen, respectively. For the mixed chemical and biological sulfide oxidation in wastewater, Wilmot et al. (7) reported reaction orders of 0.6–1.2 for sulfide and 0.2 for DO.

Factors Influencing Stoichiometry and Kinetics. Several factors are known to influence both the stoichiometry and the kinetics of chemical sulfide oxidation in aqueous solutions. These factors include the sulfide to oxygen ratio, the reactant concentrations, pH, temperature, ionic strength, and presence of catalysts or inhibitors (10, 13, 15). Several of these factors are subject to significant variability in wastewater of sewer networks.

The stoichiometry of the oxidation processes is influenced by the ratio between the reactants. In general, the literature indicates that excess oxygen favors products with sulfur in a high oxidation state, whereas oxygen limitation favors less oxidized sulfur species (14, 15). In addition to the ratio between the reactants, their concentration has also been found to influence the product distribution (15).

The rate of chemical sulfide oxidation has been shown to increase with the reactant concentrations. This finding has been confirmed for different matrixes including buffer solutions, seawater, and wastewater. With respect to in-sewer processes, relatively low concentrations of reactants are most commonly found. Under typical conditions, the oxygen concentration rarely exceeds 50% saturation and is usually much lower when sulfide and DO coexist. Typically, the sulfide concentration will increase with decreasing DO concentration. Sulfide concentrations of 0.5, 3, and 10 g of S m^{-3} may be considered as low, moderate, and high, respectively (2).

The pH dependency of the kinetics of chemical sulfide oxidation in acidic and mildly alkaline solutions is generally agreed on in the literature. Within the pH range typical for municipal wastewater (i.e., pH 6–8), the rate of sulfide oxidation has been shown to increase with pH (13, 17). The rate of chemical sulfide oxidation increases with temperature. For the chemical oxidation of sulfide, the energy of activation has been reported at 33.5 and 57 kJ mol^{-1} , which corresponds to a doubling in the rate with a temperature increase of approximately 14 and 8°C , respectively (17, 18). A few studies focus on the effect of ionic strength on the rate of chemical sulfide oxidation. Chen and Morris (13) did not find any effects attributable to the ionic strength. Contrary to this, both Millero et al. (17) and O'Brien and Birkner (15) reported a significant increase in the sulfide oxidation rate with increasing ionic strength. This discrepancy is probably explained by the investigated range of ionic strengths. The work by Chen and Morris (13) was performed at relatively low ionic strengths ($<0.2 \text{ M}$) whereas both Millero et al. (17) and O'Brien and Birkner (15) investigated a broad range of ionic strengths, 0–6 and 0.155–1.78 M, respectively. However, the conductivity of domestic wastewater is typically between 700 and $1200 \mu\text{S cm}^{-1}$, which according to the U.S. EPA approximates ionic strengths between 0.009 and 0.016 M (6, 19). Considering the reported effects of ionic strength on oxidation kinetics, no significant effects are expected in domestic wastewater.

It is generally accepted that the chemical oxidation of sulfide is highly susceptible to catalysis and inhibition. Even trace concentrations of certain metals increase the reaction rate significantly (12). Chen and Morris (10) studied the catalytic and inhibitory effects of a variety of metals and organic substances. They found all the metal ions tested to catalyze the oxidation process whereas the organic substances were found to possess either catalytic or inhibitory effects. Several of the organic substances they tested are commonly found in wastewater (e.g., urea and citrate). They also found the stoichiometry to change when the oxidation process was catalyzed or inhibited, although no general guidelines were given.

In wastewater, high concentrations of organic matter are present. The organic matter is comprised of a wide array of different organic substances, which may catalyze or inhibit the chemical oxidation of sulfide (10). For this reason, a detailed understanding of the effects of wastewater organic matter is difficult to achieve. When comparing the reported kinetics of chemical sulfide oxidation in wastewater to kinetics reported for buffered water, the kinetics in wastewater is generally faster (7–9, 13). However, owing to a large discrepancy in the reported kinetics of chemical sulfide

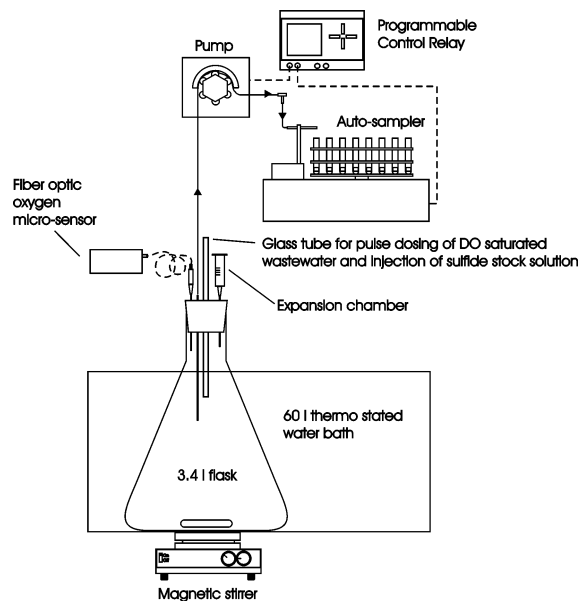


FIGURE 1. Diagram of the experimental setup for studying sulfide oxidation in wastewater. Pathways for sampling (full lines) and electronic wiring (dashed lines) are indicated.

oxidation in buffered water, it is not possible to be conclusive on the effect of wastewater constituents.

Oxidation of sulfide will either produce or consume hydrogen ions or act neutral, depending on the products, as shown in eqs 1–4. For that reason, buffers have been widely employed in order to maintain constant pH during the course of the experiments. Chen and Morris (13) found phosphate buffer to catalyze the sulfide oxidation significantly in experiments where the sulfide concentration was less than $6.4 \text{ g of S m}^{-3}$. Consequently, the use of phosphate buffers in combination with relatively low concentrations of sulfide prevents the experimental results to be extrapolated to other systems. Such effects have not been reported for other buffers.

Experimental Section

Experimental Setup. The kinetics and stoichiometry of chemical sulfide oxidation in wastewater originating from a sewer network was investigated using a batch reactor operated with manual pulse dosing of sulfide and DO. The experimental setup is depicted in Figure 1. The reactor was a 3-L Erlenmeyer flask (3.4 L total volume), which was completely filled. The wastewater was buffered using PA (Pro Analysis) grade Tris buffer [$\text{NH}_2\text{C}(\text{CH}_2\text{OH})_3 + \text{NH}_2\text{C}(\text{CH}_2\text{OH})_3$, HCl; Calbiochem] at pH 8. The buffer concentration was 0.005 M. Conductivity (25 °C) in the wastewater prior to addition of buffer was typically in the range of 1000–1200 $\mu\text{S cm}^{-1}$. This approximates ionic strengths of 0.014–0.016 M (6). From addition of 0.005 M Tris buffer, the ionic strength changed only slightly ($\approx 15\%$). No significant effect of ionic strength was therefore expected from addition of the buffer.

The reactor was sealed with a rubber stopper, which was penetrated by a glass tube for changing part of the reaction medium and injection of a sulfide stock solution. Furthermore, a needle connecting the reactor volume to an expansion chamber and a tube for automatic sampling penetrated the rubber stopper. The reactor was placed in a thermostated water bath. During each experiment, the temperature was kept constant at $20 \pm 0.1 \text{ }^\circ\text{C}$ using a PID (proportional integral derivative) regulated heater (Heto HMT 200) and a continuously operated circulation cooler.

Wastewater was collected from a sewer line in the city of Frejlev, Denmark, during the period from March 2002 to September 2002. The upstream catchment area serves

approximately 2000 inhabitants and is without significant industries (20). Samples were collected using a bucket while avoiding scraping off sewer biofilm from the sewer pipe. All samples were collected at dry weather flow conditions at weekdays between 08:30 a.m. and 09:00 a.m. During sampling, the flow was relatively constant at approximately $4\text{--}5 \text{ L s}^{-1}$. Immediately after being collected, the samples were brought back to the laboratory and prepared for experiments.

Experiments were conducted using sterilized wastewater. The wastewater was sterilized by autoclaving at $121 \text{ }^\circ\text{C}$ for 20 min, thereby depressing biological activity. The wastewater was settled for 15 min before autoclaving, thus preventing clogging of the sampling tube. A loss of particulate organic matter and other particulate substances (e.g., silt) results from the settling process. This may have an effect on the chemical oxidation rate of sulfide as the particulate matter may possess either catalytic or inhibitory properties. However, initial experiments on settled and unsettled wastewater from a single sample had shown that the effect of settling was negligible. Therefore, the measured rates of chemical sulfide oxidation are expected to be consistent with rates of chemical sulfide oxidation in unsettled wastewater during transport in sewers networks.

Before starting an experiment, wastewater was added to the reactor, and buffer salts were dissolved. An initial DO concentration of approximately $4 \text{ g of O}_2 \text{ m}^{-3}$ was reached by bubbling either nitrogen or oxygen gas through the wastewater. When the desired DO concentration was attained, the rubber stopper was put in place, and the experiment was ready to start. Before starting the experiments, the DO concentration was monitored for a period of roughly 1 h to ensure that the DO concentration was stable.

The experiments were started by introducing sulfide from a sulfide stock solution through the glass tube. Initial sulfide concentrations ranged from 8 to 10 g of S m^{-3} . Sulfide stock solutions were prepared regularly by dissolving appropriate amounts of PA grade sodium sulfide ($\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$; Merck) in demineralized, deoxygenated water. Deoxygenated water was prepared by flushing demineralized water with nitrogen gas of high purity for 15 min, thereby attaining DO concentrations less than $0.1 \text{ g of O}_2 \text{ m}^{-3}$. Experiments were run until DO was depleted, then oxygen was supplied to the wastewater, and the experiment continued. DO was supplied by changing part ($\approx 10\%$) of the reaction medium with buffered oxygen-saturated wastewater. This was done by removing wastewater from the reactor through the glass tube, using a syringe, while at the same time pouring buffered oxygen-saturated wastewater into the expansion chamber. That way, it was possible to change part of the reactor volume almost instantaneously without removing the rubber stopper. The oxygen concentration was typically depleted 2–3 times during the course of one experiment.

With a frequency of 4 h^{-1} , an autosampler collected 0.5 mL of sample in test tubes. The samples were preserved until analysis by precipitation of the sulfide as zinc sulfide (ZnS), which is highly impervious to oxidation (21). This was achieved by pipetting 1.0 mL of 10% zinc acetate solution into each test tube prior to the experiment.

The presence of metal surfaces exposed to the reaction medium was minimized to avoid possible heterogeneous catalysis of the oxidation reaction. Accordingly, the tip of the needle inside the reactor was covered with Tygon tubing, and samples were collected through a tube made of Peek. To verify that the experimental setup did not catalyze the reaction, initial experiments on sulfide oxidation in buffered water were conducted using the experimental setup described above. These experiments gave results comparable to literature values on noncatalyzed sulfide oxidation (13, 17).

Analytical Procedures. The total sulfide concentration in the samples was determined according to the methylene

blue method of Cline (22). The use of an ion-selective electrode (ISE) for monitoring the sulfide concentration was considered; however, Millero et al. (17) showed that faster oxidation rates were obtained from sulfide analysis by ISEs as compared to determination by the methylene blue method and accordingly discouraged the use of sulfide ISEs for studying sulfide oxidation. The oxygen concentration was determined using a PreSens Microx TX2 oxygen meter and a fiber optic oxygen microsensor. The working principle of fiber optic oxygen microsensors is based on quenching of luminescence caused by collision between molecular oxygen and luminescent dye molecules in the excited state. The luminescent dye molecules are immobilized in a polystyrene matrix at the tip of an optical fiber with a diameter of 140 μm . The fiber optic oxygen sensor has several advantages over conventional Clark-type sensors. These include no analyte consumption, no stirring sensitivity, superior stability, and no sensitivity for sulfide (23). Therefore, fiber optic oxygen sensors are considered ideal for measuring DO in aqueous solutions containing sulfide. The ionic strength was measured as conductivity using a Struers Knick Konduktometer 702, and the pH was measured using a Mettler Toledo pH transmitter 2400 in combination with a Hamilton Polylyte Pro pH electrode.

Oxidation Kinetics and Stoichiometry. The oxidation kinetics was calculated from the sulfide and DO concentrations versus time using a central difference formula of order $O(h^4)$ according to Mathews (24). This approach allowed the kinetics to be calculated continuously at varying reactant concentrations during the course of the experiments. The kinetic parameters were determined by simulation using the rate equation given in eq 5 (i.e., by repeated simulation of experimental results until the best agreement between simulations and measurements were achieved). Simulations of the measurements were performed according to Euler's method (24).

The stoichiometry was assessed in terms of the reaction coefficient defined by Cline and Richards (14):

$$R_{C,\text{chem}} = \frac{a}{b} \quad (6)$$

where $R_{C,\text{chem}}$ is the reaction coefficient [$\text{mol of S (mol of O}_2\text{)}^{-1}$] and a and b are stoichiometric coefficients (i.e., $a\text{HS}^- + b\text{O}_2 \rightarrow \text{products}$).

Equations 1–4 correspond to reaction coefficients of 2, 1, 0.67, and 0.5, respectively. The reaction coefficient ($R_{C,\text{chem}}$) was explicitly found as the slope of total sulfide versus DO. The slope was determined by linear regression.

Variability and Reproducibility. The variability in stoichiometry and kinetics was evaluated by conducting experiments on a group of 25 independent samples from the same site.

To verify the reproducibility of the experimental results, triplicate experiments were conducted on a single wastewater sample. In each experiment, stoichiometry and kinetic parameters were determined independently. From these experiments, the precision of the method was calculated in terms of the standard deviation. To assess whether the precision was adequate to establish the natural variability in sulfide oxidation kinetics and stoichiometry, the variability within the single sample was compared to the variability among the group of samples.

Oxidation of Intermediates. As the chemical oxidation of sulfide typically produces intermediates that are oxidized at a slower rate than sulfide, these intermediates accumulate depending on the rate with which they are oxidized. This results in a change in the stoichiometry during the course of an experiment. To assess whether the stoichiometry changed and the oxidation rates of the intermediates were

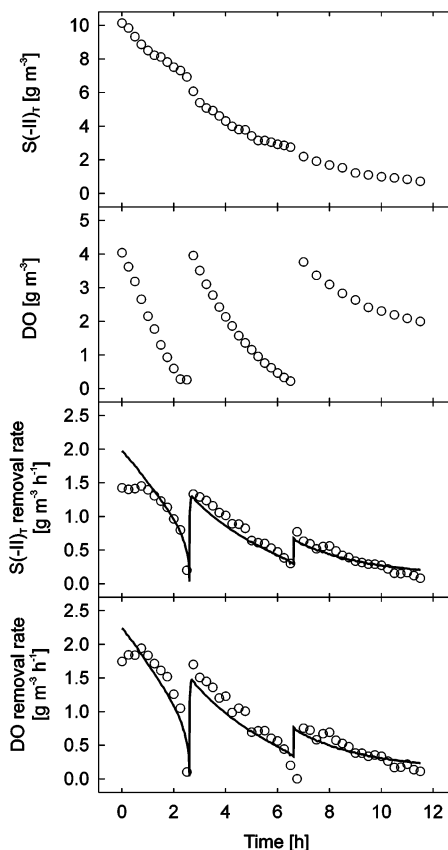


FIGURE 2. Results from a typical chemical sulfide oxidation experiment. The two top graphs show sulfide and DO concentrations vs time, and the two bottom graphs show the removal rates of sulfide and DO. The rate equation (eq 5) with the set of parameters giving the best agreement with the calculated sulfide and DO removal rates is indicated by full lines. The sulfide and DO removal rates were calculated as $-\Delta C/\Delta t$ using a central difference method.

significant, experiments with addition of a small amount of sulfide to air-saturated wastewater were conducted. In these experiments, the sulfide concentration was depleted while DO was still present. Further oxidation of intermediates would then give rise to oxygen consumption after the sulfide was depleted.

Results and Discussion

Sulfide Oxidation. Figure 2 shows the results from a single experiment with two additions of oxygen-saturated wastewater. The rate equation with the set of parameters giving the best agreement with the measurements is also depicted. The results demonstrate that the rate of chemical sulfide oxidation depends significantly on the reactant concentrations. Figure 2 also shows that a constant oxidation rate exists during the first hour of the experiment. This may be caused by an induction period reported in some studies (13, 14). Such constant initial oxidation rate was only observed in some of the experiments. From the data on sulfide concentration versus time, it was possible to calculate oxidation kinetics continually during the course of the experiment, even at such low DO concentrations ($<1 \text{ g of O}_2 \text{ m}^{-3}$) often found in the wastewater of sewer networks. The rate equation could successfully describe the chemical sulfide oxidation kinetics both at high and low reactant concentrations; however, the constant initial sulfide oxidation rate could not be described by the equation.

The oxygen removal rate from chemical sulfide oxidation in wastewater is significant as compared to the oxygen uptake from the heterotrophic biomass in wastewater of sewer

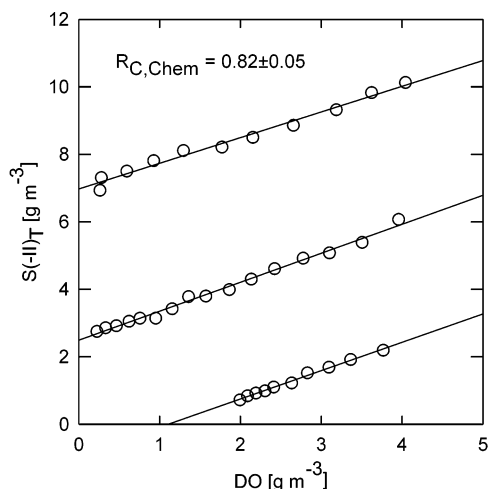


FIGURE 3. Determination of the reaction coefficient ($R_{C,chem}$) from the experiment on sterilized wastewater also shown in Figure 2. Total sulfide vs DO concentrations are shown together with linear regression lines for determination of the slope (i.e., $R_{C,chem} = \Delta S(-II)_T / \Delta O_2$).

networks. Under oxygen nonlimiting conditions, aerobic respiration by the heterotrophic biomass in the bulk water typically accounts for oxygen removal rates in the range of 2–20 g of O_2 m^{-3} h^{-1} (2). Under conditions where DO is nonlimiting for heterotrophic processes, the oxygen consumption from sulfide oxidation may be of the same order of magnitude as that of heterotrophic respiration in wastewater with a low biological activity.

The $R_{C,chem}$ was determined for each experiment by eq 6. Figure 3 shows the explicit determination of the reaction coefficient from total sulfide versus DO concentrations in the experiment shown in Figure 2. The reaction coefficient was found at 0.82 and apparently constant throughout the experiment.

Experiments with addition of a small amount of sulfide to air-saturated wastewater supported the fact that the stoichiometry could be considered constant within the time relevant to sewer processes (i.e., corresponding to the residence time of the wastewater in sewer networks). When sulfide was depleted in these experiments, the oxygen removal rate was essentially zero; thus, further oxidation of intermediates proceeded at a slow rate. This fact is in agreement with findings by Fischer et al. (11) and O'Brien and Birkner (15). The slow oxidation of intermediates was also confirmed in experiments with addition of sulfite and thiosulfate instead of sulfide. Thiosulfate and sulfite are the most commonly observed intermediates, and their formation agrees well with the reaction coefficients of 0.8–0.9 (15). From the reaction coefficients determined, it could be concluded that all the sulfide was not exclusively oxidized to a single reaction product. Monitoring pH in a series of experiments on unbuffered wastewater showed that the pH decreased 0.1–0.2 units during an experiment. Calculations of the observed pH change were in accordance with thiosulfate being the main reaction product (eq 2) and the remaining sulfide being oxidized to sulfite or sulfate (eqs 3 and 4). This finding was consistent with studies on sulfide oxidation in other matrixes (13–15).

Variation and Reproducibility. Determinations of $R_{C,chem}$ in 25 independent wastewater samples (among samples) and in a triplicate experiment (within sample) showed that the reaction coefficient exhibited only small variability. Among samples from the same site, the mean value and the standard deviation of the reaction coefficient was 0.83 and 0.07 g of S/g of O_2 , respectively. Within a single sample, the mean value of the reaction coefficient was 0.89 g of S/g of O_2 with

TABLE 1. Parameters for Chemical Sulfide Oxidation in Wastewater at pH 8.0 and 20 °C

parameter	among samples		within sample	
	mean	SD	mean	SD
k	0.25	0.05	0.27	0.03
α	0.82	0.12	0.83	0.04
β	0.20	0.09	0.21	0.08

^a Mean values and standard deviation of kinetic parameters among 25 wastewater samples and within a group of 3 wastewater samples from Frejlev, Denmark, are given.

a standard deviation of 0.08 g of S/g of O_2 ; thus, the standard deviation within triplicate determinations on the single sample was of the same order of magnitude as that in the group of 25 samples. Accordingly, variations in the stoichiometry among the 25 samples were not statistically significant. The reaction coefficients are in agreement with the reported reaction coefficient of 0.74 by O'Brien and Birkner (15), who investigated the oxidation of sulfide in buffered water at pH 7.55.

The variability of the kinetic parameters among and within samples is shown in Table 1. All the kinetic parameters were generally found to exhibit a high degree of constancy. The standard deviation of the kinetic parameters among the samples was of the same order of magnitude as the precision of the method evaluated in terms of the standard deviation of the kinetic parameters within the single sample. α was the only parameter found to exhibit variability significantly higher than the precision of the method. Similar characteristics of α have been reported in the literature; however, the reason for this finding is not known (7).

The kinetic parameters agree with the findings by Wilmot et al. (7), who investigated the mixed chemical and biological sulfide oxidation in wastewater where the biological sulfide oxidation, on average, was found to account for less than 40% of the total oxidation. They found the reaction order, on average, to be 0.75 and 0.23 with respect to sulfide and DO, respectively. It is not possible to compare the reaction rate constants as they did not evaluate the reaction rate constant in terms of a rate equation similar to eq 5. However, they presented data showing initial sulfide oxidation rates at DO concentrations of 18 g of O_2 m^{-3} and sulfide concentrations ranging from 2 to 8 g of S m^{-3} . At a sulfide concentration of 8 g of S m^{-3} , they found the mixed chemical and biological sulfide oxidation rate to be 3.7–19.7 g of S m^{-3} h^{-1} . This should be compared to a calculated oxidation rate of 2.5 g of S m^{-3} h^{-1} in wastewater from Frejlev (i.e., the oxidation rate in wastewater from Frejlev is lower but of the same order of magnitude).

The parameters differ, however, significantly from reported values for the chemical oxidation of sulfide in buffered water and seawater (13–15, 17). Specifically, the reaction rate constant is significantly higher. This is explained by the catalytic effects of wastewater constituents. The reaction order with respect to each reactant is conversely lower with an overall reaction order of around 1 in comparison to reported values of approximately 2 for sulfide oxidation in buffered water or seawater.

Previous studies on chemical sulfide oxidation have primarily been based on batch experiments in which the kinetics has been evaluated by the isolation method. In the isolation method, the reaction orders with respect to the reactants are determined by conducting experiments where each reactant is in turn kept in excess while different initial concentrations of the other reactant are employed. The concentration of the reactant in excess is essentially constant during the initial stage of the reaction, and the kinetic dependency on the reactant being employed at different

concentrations can be determined. To facilitate a successful model description of such experiments, the rate equations must be valid for a considerable range of sulfide to DO ratios. This may not be true, as the reaction mechanism and the kinetic parameters may change with varying reactant concentrations. Evidence of this was given in the study by Millero et al. (17), who found the reaction order with respect to sulfide to increase from 0.6–0.8 at 1 g of S m⁻³ to 1.0–1.2 at 6 g of S m⁻³. Similarly, Cline and Richards (14) reported that they could not find any specific rate equation, which predicted the entire temporal course of the reaction. Further evidence was given by Buismann et al. (16), who reported the reaction order of oxygen to be dependent on the sulfide concentration. However, in some studies, for example, Chen and Morris (13), a good constancy of the kinetic parameters determined at various reactant concentrations has been reported. Also, it should be noted that the considerable range of sulfide to DO ratios employed in the isolation method does not reflect the natural variation of reactants. The parameters presented in Table 1 are all found from simulation of sulfide concentrations during the course of entire experiment (i.e., the parameters represent average values valid for chemical sulfide oxidation at varying sulfide to DO ratios similar to those found in wastewater of sewer networks).

Evaluation of the Method. It has been demonstrated that the proposed method for determination of kinetics and stoichiometry of chemical sulfide oxidation in wastewater of sewer networks produces consistent results even at low DO concentrations. Experimentally determined parameters agreed well with literature values of parameters for sulfide oxidation in wastewater. All parameters were found to be relatively constant in wastewater from a single sampling site. However, literature suggests that the parameters are site specific; particularly the rate constant is subject to significant variability for wastewater from different sites (7). For determination of kinetic parameters, continuous determination of chemical sulfide oxidation kinetics and stoichiometry present an improvement over the widely used isolation method in which the kinetic parameters are evaluated on the basis of concentration levels of reactants significantly different from those found in wastewater. Moreover, continuous determination of chemical sulfide oxidation kinetics and stoichiometry enables rate equations to be established in a single experiment making the method more convenient than the isolation method.

The experimental findings clearly illustrate that chemical sulfide oxidation is an important process in the DO mass balance in sulfide-containing wastewater of sewer networks. The reaction kinetics was found to be relatively independent of the DO concentration as indicated by the low reaction order with respect to oxygen. Thus, the process will be important even at low DO concentrations, which typically prevail in wastewater of sewer networks (e.g., at DO concentrations of 0.1 g of O₂ m⁻³ the rate will be approximately 65% that at DO concentrations of 1 g of O₂ m⁻³).

From an engineering point of view, the proposed method can be used to establish kinetics and stoichiometry of chemical sulfide oxidation for sewer process modeling. Experimentally determined parameters are often site specific, and it is therefore advisable to characterize the sulfide

oxidation kinetics and stoichiometry of the wastewater of interest. For this characterization, the proposed method is capable of establishing kinetic parameters of chemical sulfide oxidation within the range reported for wastewater (7, 8).

The incorporation of chemical sulfide oxidation in sewer process models will pave way the for such models to be important engineering tools for managing sulfide formation and its effects in sewer networks. However, the biological sulfide oxidation potential together with the sulfide emission and precipitation processes needs further scientific attention in order to facilitate a full incorporation of the sulfur cycle in sewer process models.

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