# Kinetics and Stoichiometry of Aerobic Sulfide Oxidation in Wastewater from Sewers—Effects of pH and Temperature

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ABSTRACT: Kinetics and stoichiometry of aerobic chemical and biological sulfide oxidation in wastewater from sewer networks were studied. In this respect, the effects of temperature and pH were investigated in the ranges 10 to 20°C and 5 to 9, respectively. The temperature dependency of sulfide oxidation kinetics was described using an Arrhenius relationship. The effect of pH on the rate of chemical sulfide oxidation is related to the dissociation of hydrogen sulfide (H<sub>2</sub>S) to hydrogen sulfide ion (HS<sup>-</sup>), with HS<sup>-</sup> being more readily oxidized than H<sub>2</sub>S. Biological sulfide oxidation exhibited the highest rates at ambient wastewater pH, and the reaction was inhibited at both low and high pH values. Chemical sulfide oxidation was found to produce thiosulfate and sulfate, while elemental sulfur was the main product of biological sulfide oxidation. Based on the investigations, general rate equations and stoichiometric constants were determined, enabling the processes to be incorporated to conceptual sewer process models. Water Environ. Res., 78, 275 (2006).

**KEYWORDS:** wastewater, sulfide, sulfide oxidation, kinetics, rate equation, stoichiometry, pH, temperature.

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### Introduction

The occurrence of sulfide in sewer networks has traditionally been of major concern, as it is associated with several problems. Hydrogen sulfide gas (H<sub>2</sub>S) present in the sewer atmosphere can be adsorbed onto the moist sewer walls and be oxidized to sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) in a series of chemical and biological reactions (Sand et al., 1987). The sulfuric acid may subsequently react with cement in concrete sewer pipes, resulting in concrete corrosion. In severe cases, the corrosion can amount to several millimeters per year; thereby significantly reducing the expected lifetime of concrete sewer structures (Boon, 1995; Mori et al., 1991; Sand et al., 1987). Owing to its toxic properties, occurrence of hydrogen sulfide gas in the sewer atmosphere also poses safety hazards to sewer workers (ASCE, 1989). In addition, hydrogen sulfide gas is recognized as a major contributor to obnoxious odors released from wastewater collection and treatment systems (Boon, 1995). Sulfide concentrations of 0.5, 3, and 10 g S m<sup>-3</sup> in the wastewater may be considered as low, moderate, and high, respectively, in terms of problems that are typically reported (Hvitved-Jacobsen, 2002).

Sulfide in sewer networks originates primarily from sulfate reduction taking place within anaerobic regions of the biofilms and sediments covering the permanently wetted sewer walls (Norsker et al., 1995). From the biofilms and sediments, the sulfide may diffuse into the flowing wastewater, where it can be further transformed. If dissolved oxygen (DO) is present in the wastewater, the sulfide may be oxidized either chemically or biologically (Pomeroy

and Parkhurst, 1977). In addition, the sulfide may react with metals present in the wastewater and form insoluble metal sulfides (Jameel, 1989). In partly filled (gravity) sewers, a significant fraction of the sulfide may be released to the overlaying atmosphere. The emission is particularly important in areas of high turbulence (ASCE, 1989).

Because of the problems associated with the occurrence of sulfide in sewer networks, several models for evaluating potential sulfide buildup have been developed for both pressure and gravity sewers (e.g., Boon and Lister, 1975; Pomeroy and Parkhurst, 1977; Thislethwaythe, 1972). However, all of these models are empirical and, as such, must be applied with caution. More recently, numerical sewer process models based on a conceptual understanding of in-sewer chemical and biological processes have been developed (Hvitved-Jacobsen et al., 1999 and 2000; Tanaka et al., 2000). Such models allow a detailed description of changes of carbon and sulfur compounds in wastewater during transport. Although sulfide oxidation in aerobic wastewater is believed to be a major process in the sulfur cycle in sewer networks, it has only received little scientific attention in previous years. Recently, kinetics of chemical sulfide oxidation in wastewater have been studied in detail (Nielsen et al., 2003 and 2004). However, kinetics of aerobic biological sulfide oxidation in wastewater is not welldocumented, and the current extent of knowledge does not allow the process to be included in conceptual sewer process models.

The objectives of this study were to determine the kinetics and stoichiometry of chemical and biological sulfide oxidation in wastewater of sewer networks and to propose general rate equations and stoichiometric coefficients that will enable the processes to be included in conceptual sewer process models. Furthermore, it was the objective to investigate the effects of pH and temperature on the oxidation kinetics and to evaluate the variability of oxidation kinetics in different wastewater types.

# Methodology

**Sample Collection.** Wastewater samples (25 L) were collected at Frejlev sewer research and monitoring station, Denmark, and at Aalborg East and Aabybro wastewater treatment plants (WWTPs), Denmark. Samples from Frejlev were collected directly from a downstream-located sewer pipe, and samples from Aalborg East and Aabybro were primary influent collected at the inlet pumping station. All samples were collected during dry weather conditions on weekdays between 8:00 a.m. and 9:00 a.m. and transported back to the laboratory within 30 minutes of sampling.

The characteristics of the catchments of the three sampling sites differ significantly. In Frejlev, the catchment area upstream of the sampling site serves approximately 2000 person equivalents (PE),

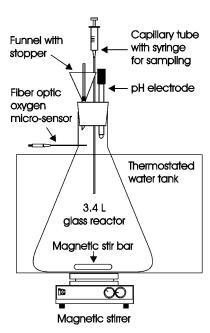


Figure 1—Experimental setup used for studying sulfide oxidation kinetics in wastewater.

and the average slope of the catchment area is relatively steep. The sewer network in Frejlev includes a single short pressure main and is without industrial inputs. Aalborg East WWTP receives wastewater from approximately 70 000 PE, and the sewer catchment is extensive, extending 30 km south of the plant. The WWTP receives both domestic and industrial wastewater. The average slope of the sewer catchment is relatively low, and several long pressure mains exist in the catchment. Aabybro WWTP receives wastewater from approximately 10 000 PE, of which approximately 1000 PE is industrial wastewater originating from a dairy. The wastewater from Aabybro is rather diluted as a result of infiltration of groundwater. Similar to the catchment of Aalborg East WWTP, the average slope of the catchment of Aabybro WWTP is relatively low, and a significant fraction of the wastewater undergoes pumping.

Experimental Setup. Sulfide oxidation experiments were conducted using a completely filled (3.4-L) batch reactor operated with pulse dosing of DO and sulfide (Figure 1). The DO was pulse dosed by aerating the reactor volume with high purity oxygen gas (O<sub>2</sub>) for 1 to 2 min; thereby attaining DO concentrations of 4 to 8 g O<sub>2</sub> m<sup>-3</sup>. Sulfide was pulse dosed by introducing a sulfide stock solution to a final concentration of approximately 10 g S m<sup>-3</sup>. Sulfide stock solutions were prepared regularly by dissolving appropriate amounts of disodium sulfide (Na<sub>2</sub>S; Merck, Germany) in demineralized, deoxygenated water. Samples for sulfide analysis were withdrawn from the center of the reactor using a syringe connected to a capillary tube made of Peek (Texloc, Fort Worth, Texas). The temperature was controlled by immersing the reactor in a thermo-stated water bath. The pH of the wastewater was adjusted using a strong monovalent acid or base (1M hydrochloric acid [HCl] or 1M sodium hydroxide [NaOH]). No buffer was added, as the pH changed only slightly during the experiments, owing to a high alkalinity of the wastewaters.

Chemical sulfide oxidation is believed to be a chain reaction and, for that reason, highly susceptible to catalysis (Chen and Morris,

Table 1—Matrix formulation of aerobic microbial and chemical transformations of DO and sulfide in batch experiments on chemical and biological sulfide oxidation at constant pH and temperature.

i	Process	S <sub>S(-II)</sub>	So	Rate equation
1	Chemical sulfide oxidation	-1	$-(R_{Cc})^{-1}$	$K_{S(-II)c}S_{S(-II)}^{mc}S_O^{nc}$
2	Biological sulfide oxidation	<b>-1</b>	$-(R_{Cb})^{-1}$	r <sub>S(-11)b</sub> *
3	Heterotrophic processes		-1	$K_H \frac{S_O}{K_O + S_O}$

<sup>\*</sup> Note: Different rate equations were evaluated.

1972b; Kuhn et al., 1983). It was therefore tested that the setup did not catalyze the sulfide oxidation reaction (Nielsen et al., 2003).

Analytical Procedures. Total sulfide was analyzed according to the methylene blue method of Cline (1969). Samples for sulfide determination were fixed in 10% zinc acetate solution and analyzed immediately after the experiments were terminated. Samples were collected with a frequency of 2 to 8 samples per hour, depending on the rate of sulfide oxidation; for example, it was attempted to obtain at least 2 samples per 1 g S m<sup>-3</sup> that was oxidized. Sulfate (SO<sub>4</sub><sup>2-</sup>), sulfite  $(SO_3^{2-})$ , and thiosulfate  $(S_2O_3^{2-})$  were analyzed by ion chromatography using a Dionex AS 11 column at a temperature of 35°C (Dionex, Sunnyvale, California). The eluent was 21 mM NaOH at a flowrate of 1 mL min<sup>-1</sup>, and the background eluent conductivity was suppressed using a Dionex ASRS-ULTRA suppressor. Samples for sulfate, sulfite, and thiosulfate determination were collected with a frequency of 1 sample per hour. The DO concentration was measured continuously using a PreSens Microx TX2 DO meter (PreSens Gmbh, Germany) in combination with a needle-type fiber optical DO sensor. The pH was measured continuously using a Hamilton Polylite Pro pH electrode (Hamilton Company, Reno, Nevada) and a Mettler Toledo MT 2400 pH transmitter (Mettler Toledo, Nänikon, Switzerland).

**Experimental Procedure.** Kinetics of chemical and biological sulfide oxidation and aerobic heterotrophic carbon transformations were determined from model simulations of measured concentrations of sulfide and DO as function of time during the experiments. Concentrations of sulfide and DO during the experiments were simulated by simultaneously solving the coupled rate equations for each process (Table 1) using the numerical Euler method. The kinetic parameters giving the best agreement between measured and simulated concentrations of sulfide and DO were determined using the least squares method. This approach determines kinetic parameters that predict the entire temporal course of the reaction.

In active wastewater containing sulfide, both chemical and biological sulfide oxidation and heterotrophic carbon transformations contribute to the DO consumption. Therefore, kinetics of heterotrophic processes were also taken into account to simulate the entire DO mass balance during the experiments. To differentiate between chemical and biological sulfide oxidation, the chemical reaction was studied in experiments using a sterilized (autoclaved) subsample of wastewater; thus, parallel experiments using both sterilized and active wastewater were conducted on each individually obtained sample.

Chemical Sulfide Oxidation. Kinetics and stoichiometry of chemical sulfide oxidation were measured according to Nielsen et al. (2003). Kinetic parameters of chemical sulfide oxidation were

determined by calibration of a rate equation simulating measured concentrations of DO and sulfide (Table 1, i=1). Kinetics of chemical sulfide oxidation in wastewater is described by a power function dependent on both reactants,  $S_{S(-II)}$  and  $S_{O}$  (Nielsen et al., 2003).

The stoichiometry of the reaction was assessed in terms of the reaction coefficient ( $R_{Cc}$ ) proposed by Cline and Richards (1969). The reaction coefficient was determined from linear regression of the change in reactant concentrations during the experiments (eq 1).

$$R_{Cc} = \Delta S_{S(-II)} / S_O \tag{1}$$

In some experiments, a range of possible oxidation products was analyzed to confirm the observed reaction coefficient.

Biological Sulfide Oxidation. Kinetics and stoichiometry of biological sulfide oxidation were determined by conducting experiments similar to the experiments on chemical sulfide oxidation, but using active wastewater instead of sterilized wastewater. In addition, kinetics of heterotrophic oxygen uptake were determined by calibration of a rate equation simulating the oxygen uptake rate (OUR) of the wastewater before introducing the sulfide stock solution. Kinetics and stoichiometry of chemical sulfide oxidation were based on parameters determined in the corresponding experiments using sterilized wastewater.

The reaction product of aerobic biological sulfide oxidation was assumed to be elemental sulfur, which is a likely process for several sulfide-oxidizing bacteria under oxygen-limited conditions (Brüser et al., 2000; Buisman et al., 1989; Norsker et al., 1995). Therefore, the reaction coefficient for biological sulfide oxidation ( $R_{Cb}$ ) was kept constant at 2 g S (g O<sub>2</sub>)<sup>-1</sup>. No efforts were made to measure the elemental sulfur concentration.

The experimental procedure described was used to study the following:

- Kinetics and stoichiometry of chemical and biological sulfide oxidation,
- · Effects of pH and temperature on oxidation kinetics, and
- Variability of sulfide oxidation kinetics between different wastewaters.

Kinetics and Stoichiometry. A series of six experiments were conducted to establish appropriate rate equations and stoichiometry of chemical and biological sulfide oxidation. These experiments were conducted at 20°C and pH 8 using wastewater from Aalborg East WWTP, which had been kept aerobic for at least 24 hours. After prolonged aeration, the initial amount of readily biodegradable substrate is consumed, and the OUR of wastewater is mainly a result of endogenous decay of the microbial biomass and transformation of slowly hydrolysable substrate (Vollertsen and Hvitved-Jacobsen, 1999). Consequently, the OUR decreases less than 5 to 10% per day (Vollertsen and Hvitved-Jacobsen, 1999). Thus, the OUR originating from heterotrophic processes could be considered constant under DO nonlimited conditions, in agreement with the model (Table 1).

To determine kinetic parameters by model calibration, a wide range of reactant concentrations should be investigated, including combinations of low and high concentrations of each reactant. This was achieved by conducting experiments with pulse dosing of sulfide and DO, in which the sulfide concentration was depleted one time, while DO was depleted two to three times.

To our knowledge, no rate equations for biological sulfide oxidation under similar conditions have been proposed. Thus, two different rate equations were tested for simulating biological sulfide oxidation: Monod type kinetics and a power equation. Monod type kinetics (eq 2) have been widely used for describing kinetics of biological processes (e.g., Henze et al., 1995a; Hvitved-Jacobsen, 2002). Power equations similar to eq 3 have been used to describe kinetics of combined biological and chemical sulfide oxidation in wastewater (Jolley and Forster, 1985; Wilmot et al., 1988).

$$r_{S(-II)b} = k_{S(-II)b} \frac{S_{S(-II)}}{K_{S(-II)} + S_{S(-II)}} \frac{S_O}{K_{OS(-II)} + S_O}$$
(2)

$$r_{S(-II)b} = k_{S(-II)b} S_{S(-II)}^{\ mb} S_O^{\ nb}$$
(3)

Where

 $r_{S(-II)b}$  = rate of biological sulfide oxidation,

 $k_{S(-II)b}$  = reaction rate constant for biological sulfide oxidation,

 $K_{S(-II)}$  = saturation constant for sulfide,

 $K_{OS(-II)}$  = saturation constant for DO,

mb = reaction order with respect to sulfide, and

nb = reaction order with respect to DO.

Effects of Temperature and pH. The effects of temperature and pH on sulfide oxidation kinetics were investigated using wastewater from Aalborg East that had been kept aerobic for an extended period. Effects of pH and temperature were determined by conducting sulfide oxidation experiments, in which the reactor was operated in a sequence of different pH levels or temperatures; for example, the pH or temperature was changed three to five times during these experiments. At each pH or temperature level, sulfide and DO was pulse dosed to identical initial concentrations of approximately 8 g S m<sup>-3</sup> and 5 g O<sub>2</sub> m<sup>-3</sup>. The oxidation kinetics at each pH or temperature level were evaluated in terms of observed reaction rate constants. The effect of temperature was investigated at temperatures between 10 and 20°C at pH 8.0. Experiments on the effect of pH were conducted at pH between 5.0 and 9.0 at 20°C. The effect of temperature on oxidation kinetics can be interpreted in terms of an Arrhenius relationship (eq 4), which traditionally has been used to describe temperature effects in activated sludge and wastewater from sewers (Henze et al., 1995a; Hvitved-Jacobsen, 2002).

$$k(T_1) = k(T_2)\alpha^{(T_1 - T_2)} \tag{4}$$

Where

 $\alpha = \text{Arrhenius constant } (-).$ 

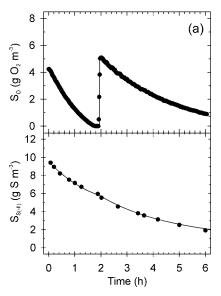
Typically,  $20^{\circ}$ C is chosen as the reference temperature ( $T_2$ ).

The effect of pH on kinetics of chemical sulfide oxidation in wastewater has been shown to correlate reasonably well with the dissociation of hydrogen sulfide, indicating that H<sub>2</sub>S is less readily oxidized than the hydrogen sulfide ion (HS<sup>-</sup>); that is, the rate increases proportionally with the proportion of sulfide present as HS<sup>-</sup> (Nielsen et al., 2004). Therefore, the overall rate of chemical sulfide oxidation can be assumed the sum of the following two reactions:

$$H_2S + n_0 O_2 \xrightarrow{k_{H_2Sc}} \text{products}$$
 (5)

$$HS^- + n_1 O_2 \xrightarrow{k_{HS^-c}} \text{products}$$
 (6)

Accordingly, at varying pH values, the rate constant for chemical sulfide oxidation can be described by eq 7 (Nielsen et al., 2004).



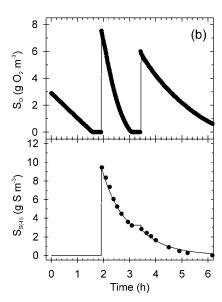


Figure 2—Measured (dots) and simulated (lines) sulfide and DO concentrations in sulfide oxidation experiments using (a) sterilized and (b) active wastewater from Aalborg East at pH 8 and 20°C.

$$k_{S(-H)c}(pH) = \frac{k_{H_2Sc} + k_{HS^-c}K_{a1}/(1/10)^{pH}}{1 + K_{a1}/(1/10)^{pH}}$$
(7)

Where

 $k_{S(-II)c}(pH)$  = overall rate constant for chemical sulfide oxidation at varying pH values.

The value of  $K_{a1}$  is  $8.913 \cdot 10^{-8}$  at  $25^{\circ}$ C (Lide, 2003).

The effects of pH on biological processes (biological sulfide oxidation and heterotrophic organic matter transformation) are described by an equation that predicts a pH range centered around an optimum pH, in which the biological processes proceed at maximum rate (eqs 8 and 9). Outside the optimum pH range, the microorganisms are inhibited and the process rates depressed.

$$k_{S(-II)b}(pH) = k_{S(-II)b}(opt. pH) \frac{\omega_{S(-II)b}}{\omega_{S(-II)b} + 10^{|opt.pH-pH|} - 1}$$
 (8)

$$k_H(pH) = k_H(opt. pH) \frac{\omega_H}{\omega_H + 10^{|opt.pH - pH|} - 1}$$
 (9)

Where

 $k_{S(-II)b}(pH)$  and  $k_H(pH)$  are the observed rate constants for biological sulfide oxidation and heterotrophic organic matter transformation as a function of pH,

 $\omega_{\rm H}$  and  $\omega_{s(-{\rm II})b}$  = pH constants that account for the width of the optimal pH range, and

Table 2—Kinetic parameters for chemical and biological sulfide oxidation in wastewater from Aalborg East. Mean values (standard deviations) of six determinations are shown.

Parameter	Chemical	Biological
$K_{S(-II)c}$ and $K_{S(-II)b}$ mc and mb nc and nb	0.370 (0.285) 1.019 (0.164) 0.171 (0.037)	0.691 (0.210) 0.906 (0.252) 0.069 (0.064)

 $k_{S(-H)b}(opt. pH)$  and  $k_{H}(opt. pH)$  are the rate constants at optimum pH values.

A similar equation was originally proposed for describing the effect of pH on aerobic biological growth (Henze et al., 1995b). Parameters for describing the effects of temperature and pH on sulfide oxidation in wastewater were determined by calibration of eqs 7 and 8 against the observed rate constants using the least squares method.

Variability of Oxidation Kinetics between Different Wastewaters. These experiments were conducted using wastewater from all three sampling sites. The experiments were started within one hour of sampling. The kinetics of both chemical and biological sulfide oxidation were evaluated in terms of an observed reaction rate constant. The pH and the temperature were kept constant at 8.0 and  $15^{\circ}$ C, respectively. Heterotrophic growth is likely to take place during the experiments as a result of growth on initially present readily degradable substrate (Bjerre et al., 1995). This will result in an increase in the OUR associated with heterotrophic carbon transformations during the experiments, which disagrees with the model description (Table 1, i = 3). However, the added sulfide was typically oxidized within one hour, and the change in heterotrophic biomass concentration during the experiments was therefore considered negligible and the OUR considered constant.

## **Results and Discussion**

**Kinetics of Sulfide Oxidation.** Measured and simulated sulfide and DO concentrations in experiments using active and sterilized wastewater from Aalborg East at pH 8 and 20°C are exemplified in Figure 2. In the experiment using active wastewater, the constancy of the heterotrophic DO uptake rate was confirmed in the absence of sulfide, for example, initially in the experiment (time < 2 hours) and again in the last part of the experiment (time > 5.5 hours).

Kinetics of chemical sulfide oxidation in wastewater was described by a power function that is approximately first order in sulfide and of lower order in DO (Figure 2a; Table 2). This is in good agreement with previous findings (Nielsen et al., 2003 and 2004). Of the rate equations tested for describing kinetics of biological sulfide

oxidation, the power equation was found to give the best agreement between the simulated and the observed concentrations (Figure 2b). When applying Monod kinetics, the saturation constant with respect to sulfide was considerably higher than the highest sulfide concentration used, which resulted in a poor determination. To determine saturation constants experimentally, they should be within the concentration range investigated. Consequently, the Monod type kinetics were found unsuitable for simulation of biological sulfide oxidation in the concentration range of sulfide investigated.

The reaction orders, with respect to sulfide (mb) and DO (nb) of biological sulfide oxidation, were not significantly different from those determined for the chemical oxidation (Table 2). For the combined chemical and biological oxidation of sulfide, Wilmot et al. (1988) proposed a rate equation that was first order in the sulfide concentration and exhibited Monod type kinetics with respect to the DO concentration. They proposed the saturation constant for oxygen to be 3 g m<sup>-3</sup>, indicating that the kinetics were highly dependant on the DO concentration in the range up to approximately 6 g O<sub>2</sub> m<sup>-3</sup> (two times the saturation constant). This finding could not be confirmed; on the contrary, the kinetics of biological sulfide oxidation were found to be relatively independent on the oxygen concentration as indicated by the low reaction order with respect to DO (Table 2). With respect to sulfide, the reaction was found to be approximately first order, which is in good agreement with the findings of Wilmot et al. (1988). The reaction rate constant for biological sulfide was higher than the rate constant for chemical sulfide oxidation. This observation is in good agreement with findings by Kontronarou and Hoffmann (1991), who found the oxidation rate in sterilized wastewater to be approximately 30% of the rate in active wastewater. Similarly, Wilmot et al. (1988) reported a 12 to 56% reduction in oxidation rate after sterilization.

In the experiments on temperature and pH effects and on variability of sulfide oxidation kinetics, the rate of both chemical and biological sulfide oxidation was simulated with reaction orders with respect to sulfide and DO of 1.0 and 0.1, respectively.

Stoichiometry of Sulfide Oxidation. The stoichiometry of chemical sulfide oxidation is complex and has been reported to result in an array of various products. The most commonly observed products and intermediates are polysulfides  $(S_n^{2-}; 2 \le n \le 5)$ , thiosulfate  $(S_2O_3^{2-})$ , sulfite  $(SO_3^{2-})$ , and sulfate  $(SO_4^{2-})$  (Chen and Morris, 1972a; Cline and Richards, 1969; Fischer et al., 1997; O'Brien and Birkner, 1977). The product distribution has been shown to depend on several factors, such as pH and the ratio between the reactants (Kuhn et al., 1983). Theoretically, the reaction coefficient  $(R_C)$  can range from 0.5 g S (g  $O_2$ )<sup>-1</sup>, when all sulfide is oxidized to sulfate, and 2 g S (g  $O_2$ )<sup>-1</sup>, when elemental sulfur is the only oxidation product (eqs 10 to 13).

$$2HS^{-} + O_2 \rightarrow 2S^{0} + 2OH^{-} \tag{10}$$

$$2HS^{-} + 2O_2 \rightarrow S_2O_3^{2-} + H_2O \tag{11}$$

$$2HS^- + 3O_2 \rightarrow 2SO_3^{2-} + 2H^+$$
 (12)

$$2HS^{-} + 4O_2 \rightarrow 2SO_4^{2-} + 2H^{+} \tag{13}$$

The reaction coefficient for chemical sulfide oxidation was determined at  $0.87 \text{ g S (g O}_2)^{-1}$ , with a standard deviation of  $0.10 \text{ g S (g O}_2)^{-1}$  in the six experiments. This is in good agreement with earlier investigations using wastewater from Frejlev, in which the reaction coefficient of chemical sulfide oxidation was on average determined at  $0.83 \text{ g S (g O}_2)^{-1}$  in 25 experiments (Nielsen et al., 2003). The reaction coefficient is also in reasonable

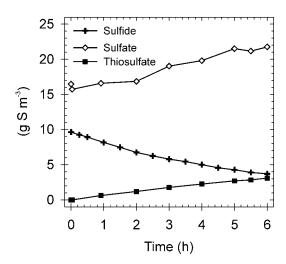


Figure 3—Measured concentrations of sulfide, sulfate, and thiosulfate in a chemical sulfide oxidation experiment.

agreement with the reported reaction coefficient of 0.74 by O'Brien and Birkner (1977), who investigated the chemical oxidation of sulfide in buffered water at pH 7.55. Product analyses revealed that sulfate and thiosulfate were the main oxidation products of chemical sulfide oxidation, in good agreement with the observed reaction coefficient (Figure 3). Previous studies have shown that the stoichiometry of chemical sulfide oxidation is constant during the course of the reaction and independent of moderate pH fluctuations (Nielsen et al., 2003 and 2004).

The assumption that the reaction product of biological sulfide oxidation was elemental sulfur fit well with the observed data. Accordingly, the reaction coefficient was kept constant at 2 g S (g  $\rm O_2$ )<sup>-1</sup>. In some experiments, however, a better simulation of the DO concentration could be achieved, assuming a lower reaction coefficient for biological sulfide oxidation of approximately 1.7 g S (g  $\rm O_2$ )<sup>-1</sup>. This can be explained by a more complex product distribution resulting from biological sulfide oxidation, such as complete oxidation of a part of the sulfide to sulfate. Another explanation may be biological oxidation of products of the chemical sulfide oxidation; for example, it is well-accepted that several sulfide-oxidizing bacteria also are capable of oxidizing thiosulfate (Brüser et al., 2000). This will affect the oxygen mass balance, resulting in a higher-than-expected oxygen consumption and a lower reaction coefficient.

Short-Term Temperature Effects on Oxidation Rates. Four experiments were made on wastewater from Aalborg East to investigate effects of temperature on kinetics of sulfide oxidation (Figure 4). Short-term temperature effects on heterotrophic processes in wastewater have been extensively studied (Vollertsen et al., 1999). Based on these studies, an Arrhenius constant of 1.10 was adopted for describing temperature effects on heterotrophic processes in the model simulations.

The effect of temperature on both chemical and biological oxidation was well-described by the Arrhenius equation (eq 4). The Arrhenius constant was determined at 1.08 (standard deviation = 0.02) for the rate of chemical oxidation and 1.10 (standard deviation = 0.03) for the rate of biological sulfide oxidation. This corresponds to a doubling of the rates with a temperature increase of 9 and 7°C, respectively; that is, the rate of chemical

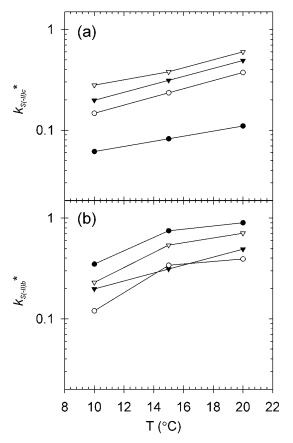


Figure 4—Effects of temperature on kinetics of (a) chemical and (b) biological sulfide oxidation in wastewater. The  $k_{S(-1))c}^*$  and  $k_{S(-1))b}^*$  are the observed oxidation rate constants.

sulfide oxidation was apparently less dependent on temperature than the rate of biological oxidation. In an earlier investigation of temperature effects on chemical sulfide oxidation, Nielsen et al. (2004) found an Arrhenius constant of 1.06 (standard deviation = 0.01) in experiments using wastewater from Frejlev. In view of this earlier investigation and taking into consideration the uncertainty of the determination, it is suggested to apply an Arrhenius constant of 1.07 for describing short-term temperature effects on chemical sulfide oxidation in sewer networks.

The results are in reasonable agreement with other investigations. For the chemical sulfide oxidation in water and seawater at 25°C and pH 8, Millero et al. (1987) reported the energy of activation to be 57 kJ mol<sup>-1</sup>, which corresponds to a doubling of the rate with a temperature increase of 8.7°C. However, for the combined chemical and biological oxidation of sulfide in wastewater, Wilmot et al. (1988) found the rate to double with a temperature increase of approximately 15°C.

It should be noted that the experiments only account for short-term temperature changes. Acclimation of the biomass to changes in temperature will inevitably yield different results. A short-term increase in temperature is expected to result in a smaller increase in the activity of the sulfide-oxidizing bacteria compared to long-term changes. Similarly, a short-term decrease in temperature will result in more pronounced decrease in the activity. Accordingly, a momentary lowering of the temperature results in an overestimation of the Arrhenius constant, whereas an increase in the temperature results in an underestimation of the Arrhenius constant

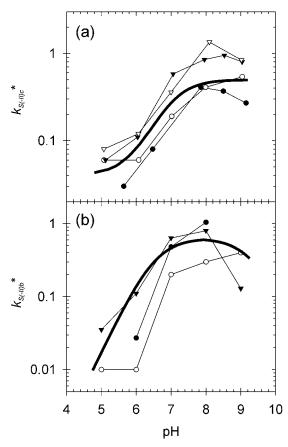


Figure 5—pH dependency of (a) chemical and (b) biological sulfide oxidation kinetics in wastewater from Aalborg East. Observed reaction rate constants,  $k_{S(-II)c}^*$  and  $k_{S(-II)b}^*$ , and a model describing the effects (eqs 7 and 8) are shown.

(Christensen and Harremoës, 1978). The combined effect of this phenomenon probably explains the concave line obtained in the experiments on temperature effects on kinetics of biological sulfide oxidation because the ambient wastewater temperature was close to 15°C (Figure 4). Short-term changes in temperature are typical for sewer systems and interactions between sewer systems and receiving waters (Vollertsen et al., 1999).

**pH Effects on Oxidation Rate.** Four experimental trials were made to investigate the effects of pH on the kinetics of sulfide oxidation. To differentiate biological sulfide oxidation from chemical sulfide oxidation, the rate of biological sulfide oxidation must be significant compared to the rate of chemical sulfide oxidation. In one experiment, the biological sulfide oxidation rate was negligible; therefore, only the results of three experiments were successful (Figure 5b). The effects of pH on heterotrophic processes in wastewater are not well-documented. Such effects were therefore also investigated (Figure 6). Because of significant differences in the activity among the experiments (OUR<sub>max</sub> ranged from 2.3 to 4.7 g O<sub>2</sub> m<sup>-3</sup> h<sup>-1</sup>), the pH dependency of the heterotrophic processes is plotted on a relative scale in Figure 6.

The effect of pH on the sulfide oxidation rate could be described by the dissociation of  $H_2S$  to  $HS^-$ , with  $H_2S$  being oxidized at a lower rate than  $HS^-$ . Kinetics of chemical sulfide oxidation at varying pH were simulated with rate constants for oxidation of  $H_2S$  and  $HS^-$  of 0.04 and 0.5 (g  $O_2$  m<sup>-3</sup>)<sup>-0.1</sup> h<sup>-1</sup>, respectively. Thus, the rate

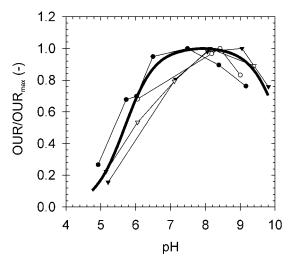


Figure 6—pH dependency of heterotrophic processes in wastewater from Aalborg East.

of chemical sulfide oxidation was significantly faster at alkaline pH than under acidic conditions. This is in fair agreement with findings from other systems. Millero et al. (1987) reported a less pronounced effect, with the rate constant for the chemical oxidation of HS<sup>-</sup> being 4.3 times faster than the rate constant for oxidation of H<sub>2</sub>S.

The results confirmed that eq 8 could be applied for describing the pH dependency of biological sulfide oxidation (Figure 5b). The equation also fit well with the pH dependency of heterotrophic processes (Figure 6). The optimum pH for both the biological sulfide oxidation and the heterotrophic processes was determined at 7.9 (Figures 5 and 6). During sampling, the pH of the wastewater from Aalborg East was, on average, 8.9; that is, the maximum rate coincided with the ambient wastewater pH, indicating that the microbial biomass was well-adapted to the ambient wastewater pH. The result is therefore considered site-specific. The pH constant,  $\omega$ , which accounts for the width of the optimal pH range, was determined at 25 and 175 for biological sulfide oxidation and heterotrophic processes, respectively. Thus, the heterotrophic bacteria oxidizing organic substrates exhibited maximum activity over a wider pH range than the sulfide-oxidizing bacteria. During the experiments, it was observed that changing the pH below 5.5 irreversibly inhibited the biomass; thus, upon increasing the pH, after being adjusted below 5.5, the activity remained low (data not shown).

Variability of Sulfide Oxidation Kinetics. In total, 12 experiments were conducted to evaluate the variability of sulfide oxidation kinetics among three different wastewaters. The in situ pH and temperature of the three wastewaters used (Table 3) were close to the conditions maintained during the experiments (pH 8 and 15°C). The kinetics of both chemical and biological sulfide oxidation were found to be highly site-specific (Table 4). In experiments using wastewater from Aalborg East and Aabybro, the kinetics of both reactions were significantly faster compared to experiments using wastewater from Frejlev. This finding was particularly evident for the kinetics of biological sulfide oxidation, which was more than one order of magnitude slower in the wastewater from Frejlev. Similar observations were made by Wilmot et al. (1988), who found the rate of combined chemical and biological sulfide oxidation to vary by a factor of four in three different wastewaters. For a given wastewater, the variability of the reaction rate constants were significant, as indicated by the relatively large standard deviations compared with the mean

Table 3—In situ pH and temperature of the three wastewaters during sampling.

	n	рН	Temperature (°C)
Aalborg East Freilev	4	7.98 (0.18) 8.37 (0.04)	14.5 (0.5) 13.6 (1.0)
Aabybro	4	7.78 (0.11)	12.1 (0.6)

values (Table 4). This finding also agrees well with the findings by Wilmot et al. (1988). The standard deviations of the reaction rate constants were larger for the biological oxidation than for the chemical oxidation. This is an artifact of the method, because the chemical reaction is determined in experiments in which the chemical reaction is isolated, whereas the kinetics of the biological oxidation is determined in experiments where both chemical and biological sulfide oxidation occur simultaneously. The error in the determination of the kinetics of biological sulfide oxidation, therefore, also includes the experimental error of the determination of the kinetics of chemical sulfide oxidation.

The faster biological oxidation rates observed in the wastewater from Aalborg East and Aabybro are possibly related to the characteristics of the sewer systems. The presence of pressure mains and the average sewer slope in these two catchments indicate the extent of reaeration in the sewer systems. In Frejlev, a steep slope combined with the absence of long pressure mains probably results in strictly aerobic conditions, whereas low slopes and the existence of several long pressure mains suggests that the wastewater from Aalborg East and Aabybro are subject to varying aerobic and anaerobic conditions during transport. In both these sewer networks, sulfide buildup has been observed. The results therefore indicate that biological sulfide oxidation is faster in wastewater that is subject to transient aerobic—anaerobic conditions during transport.

The rate constant for biological sulfide oxidation in wastewater from Aalborg East was not significantly different in the fresh wastewater compared to the wastewater subjected to prolonged aeration (Tables 2 and 4); that is, the sulfide-oxidizing biomass was apparently still viable after 24 hours aeration in the absence of sulfide.

# **General Rate Equations**

Based on the full range of experiments, a set of rate equations describing chemical and biological sulfide oxidation in aerobic wastewater from sewer networks is proposed (eqs 14 and 15).

$$r_{S(-II)c} = \frac{k_{H_2Sc} + k_{HS^-c} K_{a1} / (1/10)^{pH}}{1 + K_{a1} / (1/10)^{pH}} S_{S(-II)}^{mc} S_O^{nc} \alpha_{S(-II)c}^{T - 20^{\circ}C}$$
(14)

$$r_{S(-II)b} = k_{S(-II)b} \frac{\omega_{S(-II)b}}{\omega_{S(-II)b} + 10^{|opt.pH-pH|} - 1} S_{S(-II)}^{mb} S_O^{nb} \alpha_{S(-II)b}^{T-20^{\circ}C}$$

(15)

Table 4—Rate constants for biological and chemical sulfide oxidation in different wastewaters at pH 8 and 20°C.

Wastewater	n	$K_{S(-II)c}$	$K_{S(-II)b}$
Aalborg East	4	0.349 (0.048)	0.671 (0.106)
Frejlev	4	0.094 (0.021)	0.041 (0.059)
Aabybro	4	0.424 (0.161)	0.991 (1.014)

Table 5—Kinetic and stoichiometric parameters for chemical and biological sulfide oxidation in sewer wastewater.

Parameter	Value	Unit
mc and mb	1	(-)
nc and nb	0.1	(-)
$R_{Cc}$	0.9	$(g S (g O_2)^{-1})$
R <sub>Cb</sub>	2.0	$(g S (g O_2)^{-1})$ $(g S (g O_2)^{-1})$
	1.07	(-)
α <sub>S(-  )b</sub> *	1.10	(-)
$\alpha_{S(-l')c}$ $\alpha_{S(-l')b}^{\star}$ $\omega_{S(-l')b}^{\star}$	25	(-)

<sup>\*</sup> Note: Based on experiments with wastewater from Aalborg East only.

The equations account for effects of pH and temperature. However, kinetics of both chemical and biological sulfide oxidation are subject to significant variability among different wastewaters. Kinetic parameters should accordingly be selected with caution. The reaction rate constant is particularly subject to variability between sites (Table 4). However, significant temporal variability also exists in wastewater obtained from a single site (Tables 2 and 4). For this reason, recommended values for reaction rate constants are difficult to give. Preferably, for predicting potential sulfide buildup, investigations should be conducted using wastewater from the actual system. Several parameters can, however, be considered constant, and recommended values of these parameters are listed in Table 5.

The equations describing sulfide oxidation in the flowing wastewater—when incorporated to conceptual sewer process models—represent an improvement over previous empirical models for predicting potential sulfide buildup in sewer networks. However, sulfide can also be oxidized in the outer aerobic regions of the biofilms and sediments covering the permanently wetted sewer walls. This process has currently not been studied in detail. Nevertheless, this process may also be important in the sulfur cycle, and further studies are needed to develop a theoretically sound model concept for simulating sulfide buildup in sewer networks.

# Conclusions

Kinetics and stoichiometry of both chemical and biological sulfide oxidation in wastewater of sewer networks were investigated. General rate equations describing chemical and biological sulfide oxidation in wastewater of sewer networks are proposed. Based on the experiments, several conclusions were drawn.

- Both chemical and biological sulfide oxidation was of importance in wastewater of sewer networks.
- The pH dependency of chemical sulfide oxidation can be described by and is determined by the dissociation of H<sub>2</sub>S with H<sub>2</sub>S being oxidized at a lower rate than HS<sup>-</sup>.
- The kinetics of biological sulfide oxidation was found to be faster at a pH similar to the in situ conditions compared to the rate at lower and higher pH values.
- The temperature dependency of chemical and biological sulfide oxidation was described by the Arrhenius equation. The rate of chemical and biological sulfide oxidation was found to double with a temperature increase of 9 and 7°C, respectively.

 Kinetics of both chemical and biological sulfide oxidation was found to be subject to significant variability, both in terms of temporal variability and variability between sites. For the three wastewaters investigated, it was found that biological sulfide oxidation was most significant when the wastewater have been subjected to transient aerobic—anaerobic conditions during transport.

## **Nomenclature**

# **Dissolved Components**

 $S_O$  Dissolved oxygen (g O<sub>2</sub> m<sup>-3</sup>)  $S_{S(-II)}$  Total sulfide; i.e., H<sub>2</sub>S + HS<sup>-</sup> + S<sup>2-</sup> (g S m<sup>-3</sup>)

### Stoichiometry

 $R_{Cb}$  Reaction coefficient of biological sulfide oxidation (g S (g  $O_2$ )<sup>-1</sup>)

 $R_{Cc}$  Reaction coefficient of chemical sulfide oxidation (g S (g  $O_2$ )<sup>-1</sup>)

## Rates

 $r_{S(-II)b}$  Biological sulfide oxidation rate (g S m<sup>-3</sup> h<sup>-1</sup>)  $r_{S(-II)c}$  Chemical sulfide oxidation rate (g S m<sup>-3</sup> h<sup>-1</sup>)

#### **Kinetic Constants**

 $k_{S(-II)b}$  Rate constant for biological sulfide oxidation ((g S m<sup>-3</sup>)<sup>1-mb</sup>(g O<sub>2</sub> m<sup>-3</sup>)<sup>-nb</sup>h<sup>-1</sup>)

 $k_{S(-II)c}$  Rate constant for chemical sulfide oxidation ((g S m<sup>-3</sup>)<sup>1-mc</sup>(g O<sub>2</sub> m<sup>-3</sup>)<sup>-nc</sup>h<sup>-1</sup>)

 $k_{H_2}Sc$  Rate constant for chemical oxidation of H<sub>2</sub>S ((g S m<sup>-3</sup>)<sup>1-mc</sup>(g O<sub>2</sub> m<sup>-3</sup>)<sup>-nc</sup>h<sup>-1</sup>)

 $k_{HS^-c}$  Rate constant for chemical oxidation of HS<sup>-</sup>((g S m<sup>-3</sup>)<sup>1-mc</sup>(g O<sub>2</sub> m<sup>-3</sup>)<sup>-nc</sup>h<sup>-1</sup>)

 $k_H$  Rate constant for heterotrophic processes (g O<sub>2</sub> m<sup>-3</sup> h<sup>-1</sup>)

 $K_{S(-II)}$  Saturation constant for sulfide for biological sulfide oxidation (g S m<sup>-3</sup>)

 $K_{OS(-II)}$  Saturation constant for oxygen for biological sulfide oxidation (g O<sub>2</sub> m<sup>-3</sup>)

 $K_O$  Saturation constant for dissolved oxygen for heterotrophic processes (g  $O_2 \text{ m}^{-3}$ )

 $\it mb$  Reaction order of biological sulfide oxidation with respect to sulfide (-)

nb Reaction order of biological sulfide oxidation with respect to DO (-)

mc Reaction order of chemical sulfide oxidation with respect to sulfide (-)

nc Reaction order of biological sulfide oxidation with respect to DO (-)

 $\alpha_{S(-II)b}$  Temperature coefficient for biological sulfide oxidation (-)

 $\alpha_{S(-II)c}$  Temperature coefficient for chemical sulfide oxidation (-)

 $\omega_{S(-II)b}$  Width of optimum pH range for biological sulfide oxidation (-)

 $\omega_H$  Width of optimum pH range for heterotrophic processes (-)

## **General Environmental Parameters**

 $K_{a1}$  First dissociation constant for H<sub>2</sub>S (-)

pH pH

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