Kinetics of chemical sulfide oxidation under high dissolved oxygen levels

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Oxygen injection is commonly employed to control sulfide generation in sewer systems. The addition of oxygen creates aerobic conditions and prevents anaerobic sulfate reduction. At the same time, any sulfide that is already present gets oxidized both biologically and chemically. In order to depict the effect of oxygen injection, it is therefore necessary to understand the nature of both biological and chemical sulfide oxidation in a sewer system. From the modelling point of view, the knowledge of the rate by which sulfide is oxidized and oxygen is consumed is necessary to predict the dynamic changes caused by oxygen injection. Although several kinetic models for chemical sulfide oxidation are available in literature, these are developed either for different water matrices (Chen and Morris, 1972; O’Brien and Birkner, 1977; Buisman et al., 1990) or for normal dissolved oxygen (DO) levels up to 4 mg/L encountered in natural environments (Nielsen et al., 2004). Since pure oxygen is commonly employed in sewers resulting in elevated DO levels (up to 30 mg/L), these models may have limited applicability to sewers receiving oxygen injection.

In this paper, we report a model describing kinetics of chemical sulfide oxidation, developed based upon the results obtained from experiments with domestic wastewater. A 0.75 L closed vessel with arrangements for online pH, DO and dissolved sulfide measurement was used for the study. The reactor used in this study didn’t have any biofilm on reactor walls. Sewage filtered through 5-micron filter was used to avoid biological activities in the reactor. The experiments were conducted at room temperature (22±1°C) and pH was maintained at a constant level (~7.5).

Two series of experiments were conducted:

- In order to investigate the effect of DO on the rate of chemical sulfide oxidation, a set of batch experiments were conducted with sulfide concentration being kept relatively constant by periodic dosing of sulfide, while the DO was allowed to drop as the experiment progressed.
- Another 4 sets of experiments were conducted in which both the initial sulfide and DO concentrations were varied.

Online measurements of DO, pH and dissolved sulfide were done using pH and DO probes and a UV/VIS-based spectrometer. In order to carry out sulfur balance, measurement of sulfate, thiosulfate, sulfite and sulfide was done using ion chromatography.

The results of the first set experiment, which was aimed to find the dependency of oxidation rate on DO, are shown in Figure 1. The results suggest that the \( H_2S \) oxidation rate was independent of the DO concentration at a DO level above 5 mg/L, below which the \( H_2S \) oxidation rate decreased with decreasing DO level. Since the Monod type kinetics can explain this behaviour (Kotronarou and Hoffmann, 1991), this was used to describe the dependency of sulfide oxidation rate on DO. The results of batch experiments showed that the rate of sulfide oxidation followed a power function with respect to \( H_2S \) concentration. This is in agreement with most of the chemical sulfide oxidation model available in literature (Chen and Morris, 1972; Buisman et al., 1990; Nielsen et al., 2004). The following kinetic expression is therefore proposed for sulfide oxidation with oxygen.

\[
    r_{\text{oxi,chem}} = k_{\text{max,chem}} \times [H_2S]^\alpha \times \frac{[DO]}{K_{O_2} + [DO]}
\]

where, \( r_{\text{oxi,chem}} \) is the sulfide oxidation rate in mg S/L-h, \( k_{\text{max,chem}} \) is the rate constant, \( [H_2S] \) is the \( H_2S \) concentration in mg S/L, and \( [DO] \) is the DO concentration in mg/L.
The measurements of different sulfur species showed incomplete sulfide oxidation, as only a small fraction of sulfide was converted to sulfate (Figure 2). A significant amount of thiosulfate was produced during the experiment. Sulfur balance done by taking into account all the four measured sulfur species, namely sulfide, sulfate, thiosulfate and sulfite, show some sulfur loss. This strongly indicates the formation of intermediates possibly elemental sulfur or polysulfides. However, for simplification, thiosulfate was assumed to be the end product of sulfide oxidation and stoichiometric ratio was chosen accordingly.
The experimental data collected in the remaining 4 sets of experiments with different initial sulfide and DO concentrations was used to determine the parameters of the model through optimization using MATLAB. The parameter values thus determined yielded the following kinetic expression.

\[
r_{\text{ox,chem}} = 4.46 \times [\text{H}_2\text{S}]^{0.56} \times \frac{[\text{DO}]}{1.30 + [\text{DO}]}\]

Measured H\textsubscript{2}S and DO concentrations are compared with corresponding model results in Figure 3. As the comparison shows, the model was able to predict the change in H\textsubscript{2}S concentration reasonably well. The model proposed here for calculating the rate of sulfide oxidation as a function of DO and H\textsubscript{2}S concentrations is therefore validated.

![Figure 3](image-url)

**Figure 3.** Comparison of the model predicted and measured DO and H\textsubscript{2}S concentration

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**References:**