2.2.2 Biological Oxidation of Sulfide with Nitrate

Nitrate addition is increasingly becoming popular as a means of controlling sulfide generation in sewer systems. The addition of nitrate was previously thought to create anoxic conditions in a sewer system thereby preventing anaerobic sulfide generation. The studies done in recent years however indicate that sulfide can also be oxidized biologically with nitrate. However, the kinetics of anoxic sulfide oxidation remains largely unknown.

In order to model the effect of nitrate addition on sulfide generation in sewer system accurately, it is necessary to include anoxic sulfide oxidation as a process consuming both sulfide and nitrate. A laboratory study was therefore conducted to establish a kinetic expression for this. A series of batch experiments with different initial nitrate and sulfide concentrations were conducted and the data collected was used to determine the key model parameters and also to validate the model.

A 0.75 L laboratory reactor receiving continuous nitrate injection for a period of 9 months was used for batch experiments. The reactor was filled with fresh sewage and nitrate and sulfide were added to maintain intended initial concentrations. The contents of the reactor were kept stirred and samples were regularly withdrawn to measure NO₃ and H₂S to establish the respective profiles. The experiments were conducted at room temperature. The results of the batch experiments are presented in Figure 21.

A batch model was setup in MATLAB considering the following processes:

- 1. Heterotrophic growth of denitrifiers (consumption of both sulfide and nitrate)
- 2. Biological oxidation of sulfide with nitrate assuming the following double Monod type kinetic expression (consumption of both sulfide and nitrate)

$$r_{\text{oxi},\text{NO}_3} = k_{\text{max},\text{NO}_3} \times \frac{[\text{H}_2\text{S}]}{K_{\text{H}_2\text{S}} + [\text{H}_2\text{S}]} \times \frac{[\text{NO}_3]}{K_{\text{NO}_3} + [\text{NO}_3]}$$

The rate of nitrate consumption due to heterotrophic growth of denitrifiers was taken

from a separate batch experiment, in which only nitrate was added at the start of experiment (without the presence of sulfide). The consumption of nitrate was assumed to be due to heterotrophic growth.

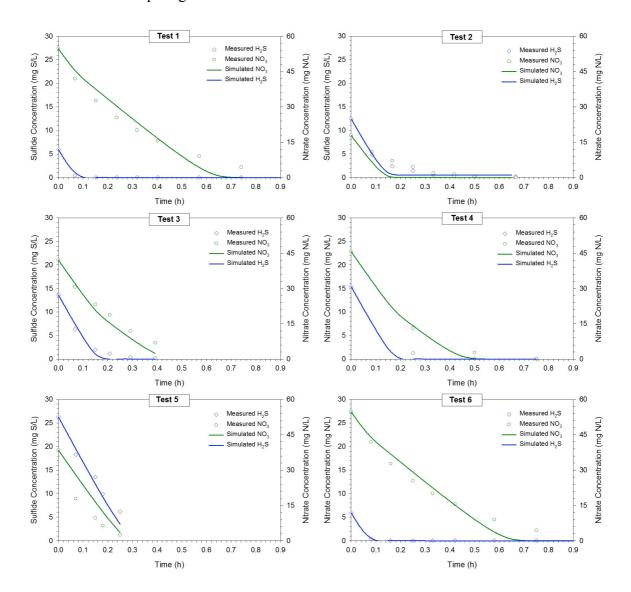


Figure 21. Comparison of the model predicted and measured NO₃ and H₂S concentrations

Data collected in six sets of experiments with different initial sulfide and NO₃ concentrations as shown in Figure 21 were used to determine the parameters of the model using MATLAB. The parameters were adjusted so as to minimize the sum of the error between the measured and the simulated values of H₂S concentration, and the results thus obtained were included in the model as follows.

$$r_{\text{oxi,NO}_3} = 102.0 \times \frac{[\text{H}_2\text{S}]}{1.0 + [\text{H}_2\text{S}]} \times \frac{[\text{NO}_3]}{0.4 + [\text{NO}_3]}$$

Where, $r_{oxi,NO3}$ is the sulfide oxidation rate in mg S/L-h, [H₂S] is the H₂S concentration in mg S/L, and [NO₃] is the NO₃ concentration in mg N/L.

The stoichiometric ratio of nitrate consumption to sulfide oxidation depends upon the end product (whether it is sulfate, thiosulfate or something else). To simplify the model and avoid large number of parameters, it was assumed that the end product of oxidation reaction is sulfate. However, the nitrate requirement was estimated based on the initial ratio of nitrate to sulfide. A higher nitrate to sulfide ratio was assumed to result in sulfate production while a lower ratio to result in elemental sulfur, thereby affecting the nitrate requirement.

Taking into account the A/V ratio of the laboratory reactor (A/V=50), the above expression is revised as follows to include the effect of A/V:

$$\begin{split} r_{oxi,NO_3} = 2.04 \times \frac{[H_2S]}{1.0 + [H_2S]} \times \frac{[NO_3]}{0.4 + [NO_3]} \times \frac{A}{V}, \text{ where 2.04 is the rate of anoxic} \\ \text{sulfide oxidation in g S/m}^2.h \end{split}$$

A comparison of the measured H_2S and NO_3 concentrations with corresponding model results is presented in Figure 21. As shown in the figure, the model was able to predict the change in H_2S and NO_3 concentration reasonably well.

The kinetic expression derived in this study will be included into both the gravity and rising main sewer models to be applied to different sewer systems. This is expected to further enhance the capability of the model in cases where nitrate is dosed for sulfide control.