2.2.1 Modeling of Sulfide Oxidation with Oxygen

Oxygen injection is commonly employed to control sulfide generation is sewer systems. The addition of oxygen creates aerobic conditions in a sewer and prevents anaerobic sulfate reduction. At the same time, any sulfide that is already present or is generated gets oxidized. In order to depict the effect of oxygen injection, it is necessary to understand the nature of both biological and chemical sulfide oxidation in a sewer system. The knowledge of the rate by which sulfide is oxidized and oxygen is consumed is necessary for the sewer model to predict the dynamic changes caused by oxygen injection. This would make the model useful in evaluating the effectiveness of oxygen injection in overall sulfide control and also designing an optimal injection strategy. Although several kinetic models are available in literature (O'Brien and Birkner, 1977; Nielsen et al., 2005; Nielsen et al., 2006), a model developed for a specific wastewater composition does not necessarily describe the phenomenon for a different wastewater matrix.

The model presented in previous PMSC meeting has been modified to improve its applicability. The results of the batch tests presented in previous report have been used for this purpose.

2.2.1.1 Conceptual Model

The results of a chemical sulfide oxidation batch test showing the changes in the concentrations of various sulfur species are shown in Figure 11. A similar trend was observed also for biological oxidation of sulfide with both nitrate and oxygen. As the results indicate, only a small portion of oxidized sulfide was actually converted to sulfate, while a major portion was oxidized to thiosulfate. An interesting finding here is that the concentrations of the oxidized sulfide species (thiosulfate, sulfite and sulfate) do not sum up to the amount of sulfide oxidized. This indicates that a substantial portion of sulfide is actually oxidized to some unknown intermediate (elemental sulfur, polysulfide etc), which is not measured in our analytical procedure. To account for this, a two step model has been hypothesized as follows.

1. The oxidation, both biological and chemical, is a two step process, sulfide being oxidized to an intermediate product first, and then the intermediate product to

sulfate. Although there is a possibility of several intermediate products, only one has been considered for simplicity of the model.

2. The first step of reaction is much faster than the second one, and hence accumulation of the intermediate product occurs. This agrees with the results of our laboratory experiments.
3. The intermediate product is reduced back to sulfide under anaerobic conditions at a rate same as the rate of reduction of sulfate to sulfide.

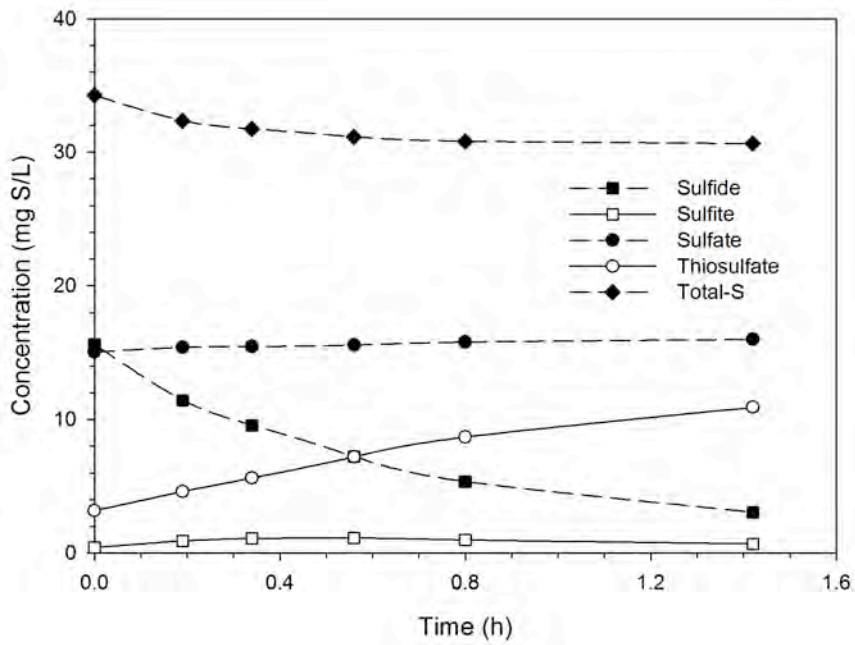

Figure 11. Sulfur balance during chemical oxidation of sulfide

2.2.1.2 Chemical Oxidation of Sulfide

In the batch tests conducted to collect the data for modeling of chemical sulfide oxidation, DO, pH and the dissolved H_2S concentrations were measured online using a pH, DO, and SCAN sensor, respectively. The H_2S signals obtained from SCAN sensor were corrected based on the correlation obtained by comparing the SCAN results with the IC measured H_2S concentration for the same sample.

The following kinetic expression was proposed for the sulfide oxidation rate as a function of the sulfide and dissolved oxygen concentrations.

Rate of oxidation of sulfide to intermediate product (S_1):

$$r_{oxi,chem,H2S\text{-}S1} = k_{max,chem,H2S\text{-}S1} \times [H_2S]^{\alpha} \times \frac{[DO]}{K_{O2} + [DO]}$$

Rate of oxidation of intermediate product (S_1) to sulfate:

$$r_{oxi,chem,S1\text{-}SO4} = k_{max,chem,S1\text{-}SO4} \times [S_1]^{\beta} \times [DO]$$

Where, $r_{oxi,chem}$ is the sulfide oxidation rate in mg S/L-h, $[H_2S]$ is the H_2S concentration in mg S/L, [S1] is the S_1 concentration in mg S/L and [DO] is the DO concentration in mg/L.

Data collected in six sets of experiments with different initial sulfide and DO concentrations were used to determine the parameters of the model through optimization using MATLAB. The parameters were adjusted so as to minimize the sum of the error between the measured and the simulated values of H_2S concentration, and the results are presented in the following table.

Parameter	Value	Determination
$k_{max,chem,H2S\text{-}S1}$	4.38 mg S/L h	Optimization
$k_{max,chem,S1\text{-}SO4}$	0.15 mg S/L h	Assumed
α	0.56	Optimization
β	1.0	Assumed
K_{O2}	2.0 mg S/L	Assumed

Furthermore, stoichiometric requirement of oxygen for the oxidation of sulfide to intermediate sulfur product was found to be 0.8 mol O_2/mol S through data fit. This value is higher than the oxygen requirement for oxidation of sulfide to elemental sulfur (0.5 mol O_2/mol S), and lower than that for thiosulfate (1.0 mol O_2/mol S). Oxygen requirement

for second step could then be estimated as the difference between the overall oxygen requirement for complete sulfide oxidation (2 mol O_2/mol S) and the requirement for the first step.

A comparison of the measured H_2S and DO concentrations with corresponding model results is presented in Figure 12. As the comparison shows, the model was able to predict the change in H_2S concentration reasonably well.

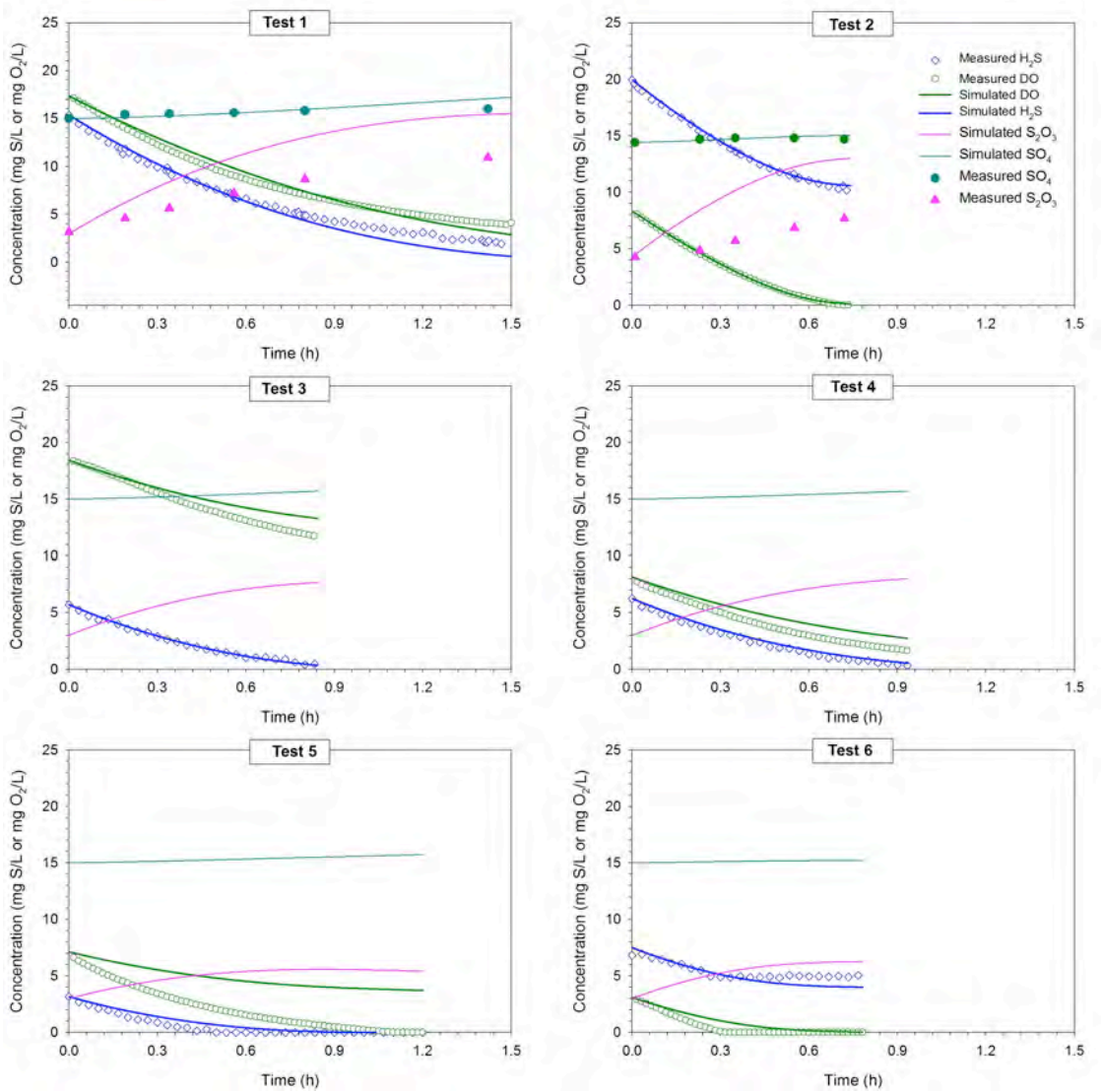

Figure 12. Comparison of the model predicted and measured DO and H_2S concentration for chemical oxidation experiments