1 Nitrate

Injection of nitrate has been one of many chemical dosing strategies applied for sulfide control in sewers. Over the last 70 years, control of hydrogen sulfide in sewers using various nitrate salts ($NaNO_3$, $Ca(NO_3)_2$, NH_4NO_3) has been reported sparsely. Nitrate, with concentration ranging from 10 to 40 mg-N/L, has been demonstrated to reduce sulfide concentration to 0.2–3 mg-S/L in rising main sewers of lengths ranging from 2.4 to 5 km.

1.1 Mechanism

Nitrate prevents the accumulation of hydrogen sulfide in sewer by the following mechanisms.

1.1.1 Oxidation of hydrogen sulfide

The oxidation of sulfide mainly occurs biologically, which takes place in the anoxic portion of the sewer biofilm. Chemical oxidation of sulfide with nitrate is possible, but the process is very slow.

Reaction mechanism and stoichiometry of biological sulfide oxidation

- Biological oxidation of sulfide is a multi step process involving a series of biochemical reactions catalyzed by micro-organisms present in sewer biofilm.

$$5S^{2-} + 2NO_3^- + 12H^+ \rightarrow 5S^0 + N_2 + 6H_2O$$
$$5S^o + 6NO_3^- + 2H_2O \rightarrow 5SO_4^{2-} + 3N_2 + 4H^+$$

- The reaction product of biological sulfide oxidation is normally the elemental sulfur and other intermediates such as thiosulfate under nitrate-limited conditions. The intermediate products are subsequently oxidized to sulfate, but the rate of this step is much lower than that of the first step.
- Actual consumption rate of nitrate for biological sulfide oxidation is reported to be lower than 0.7 g nitrate N per g S indicating a range of intermediate oxidation products.
- Kinetics of biological sulfide oxidation is described by the rate equations as follows:

$$r_{H_2S,oxidation} = k_{bio,oxi} \times \frac{[H_2S]}{K_{H_2S} + [H_2S]} \times \frac{[NO_3^-]}{K_{NO_3^-} + [NO_3^-]}$$

Further information can be obtained as follows:

- Reaction mechanism, kinetics and stoichiometry
  - Paper: Sulfur transformation in rising main sewers receiving nitrate dosage by Jiang et al. (2009)
  - Paper - Impact of nitrate addition on biofilm propertiesand activities in rising main sewers by Mohanakrishnan et al. (2009)
  - Report - Understanding the Biotransformation Processes in a Sewer System to Achieve Optimal Management

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1.1.2 Maintaining anoxic condition in bulk liquid as well as a portion of biofilm

- Sulfate reducing bacteria (SRB) are obligate anaerobes and hence are greatly affected by the presence of nitrate.
- Penetration of nitrate in biofilm is generally limited, thereby giving rise to anoxic layer in the outer part and anaerobic layer in the inner part of the sewer biofilm. Sulfide production can thus take place in anaerobic biofilm layers despite the presence of nitrate in the bulk phase.
- Sulfide produced in the anaerobic layer of the biofilm is oxidized as it diffuses out through the anoxic biofilm layer.

1.1.3 Other mechanisms

- SRB activity is hindered by competition with nitrate reducing bacteria for organic electron donors (COD).
- Nitrate addition increases the pH of the wastewater due to denitrification, which in turn decreases sulfide production.

1.2 Actions

Dosing of nitrate results into the followings:

- Oxidation of hydrogen sulfide to intermediate products such as elemental sulfur and thiosulfate and the oxidation of these intermediate products to sulfate. The second step is normally slower than the first step. The oxidation is carried out by autotrophic organisms.
- Creation of an anoxic layer on outer surface of the biofilm preventing sulfide generation in the layer. Sulfide generated in the inner anaerobic layer will diffuse out to the anoxic layer, where it will be oxidized thereby preventing its accumulation in the bulk water despite continuous production in inner anaerobic layers.
- The presence of nitrate supports the growth of heterotrophic organisms in the anoxic layer of the biofilm, thereby oxidizing the organic matter present in the wastewater through denitrification. Thus, the oxidation of both sulfide and organic matter occurs simultaneously.

1.3 Nitrate addition to sewers

Nitrate is added in either granular or liquid form, and either as a calcium or a sodium salt. Commonly used chemicals are:

- Sodium nitrate ($NaNO_3$)
- Calcium nitrate ($Ca(NO_3)_2$)
- Ammonium nitrate (NH_4NO_3)

1.4 Dosing arrangement and typical dosing rates

When nitrate is dosed to sewer, it is utilized for both sulfide and COD oxidation. The oxidation of sulfide is mainly carried out by autotrophic organisms, while the COD oxidation is carried out by heterotrophic organisms. The nitrate dosing requirement can be estimated as follows:

Nitrate demand $(gN/m^3) =$

$0.7\times$ maximum sulfide level $(gS/m^3) + NUR_{biofilm}(gN/m^2.h) \times$ HRT $(h) \times$ A/V (m^2/m^3)

It is assumed that the end product of sulfide oxidation is sulfate and the nitrate uptake rate of sewer biofilm (NUR) is constant throughout the sewer length.

When the nitrate is dosed at the wet-well of a rising main, the chemical will be depleted in few hundred meters of the pipe unless a very high concentration is used, and there will be no protection against the sulfide produced in the remaining anaerobic portion of the sewer pipe. In order to avoid this, the point of injection (POI) should be "reasonably" close to the points where sulfide control is required (Point of Control - POC). An injection site should be selected such that (1) there would be an adequate hydraulic retention time (HRT) between POI and the POC to enable the full oxidation of any sulfide present at the POI before it reaches the POC, and that (2) anoxic conditions are maintained between the two points with minimum requirement of nitrate. Increase nitrate dosing may help, but this results in consumption of VFA creating problems to downstream WWTP.

Typical nitrate dosing rate: 1.3-15.5 kg N/ML of wastewater (exact dosing rate depends upon the level of sulfide and the dosing strategy employed).

Further information can be obtained as follows:

- Dosing arrangements
  - Final Report - ARC Linkage Project on Sewer Biotransformation
- Typical dosing rate
  - Paper: Chemical dosing for sulfide control in Australia: An industry survey by Ganigue et al. (2011)

1.5 Cost of nitrate dosing

Nitrate dosing requires storage facility for the nitrate, and proper dosing facilities depending upon the type of the dosing used. Proper dosing equipments need to be installed with adequate dosing control facility.

Estimated cost of nitrate dosing is \$41.3 - \$486.6/ML (the cost depends upon the dosing rate, sulfide level and HRT in the sewer). The cost does not include the cost of chemical that may be needed for nutrient removal at the downstream WWTP.

Further information can be obtained as follows:

- Paper: Chemical dosing for sulfide control in Australia: An industry survey by Ganigue et al. (2011)

1.6 Impacts on WWTP

The added nitrate promotes denitrification in the anoxic layer of the biofilm, thereby oxidizing a significant portion of the organic matter present in the wastewater, which results in reduced levels of volatile fatty acids (VFA) in the feed to a WWTP. This will significantly affect the biological nutrient removal in the WWTP, the extent of such impact depending upon the dosing location and the rate of nitrate dosing. The addition of a readily available carbon source (for example, methanol) may be required to improve the nutrient removal performance to the same level as in the case without the nitrate dosing.

Further information can be obtained as follows:

- Paper: Integrated modelling of sewer system and wastewater treatment plant for investigating the impactsof chemical dosing in sewers by Sharma et al. (2012)

1.7 Major limitations

- Nitrate does not have an immediate or long-lasting inhibitory/ toxic effect on sulfate reduction. The nitrate dosing is only effective in controlling sulfide production when nitrate is present in the sewer. In addition to preventing sulfide from its formation, any sulfide present would be oxidized. However, nitrate dosing has no long-lasting inhibitory effect on the SRB activities. The production of sulfide resumes once the dosing is stopped.
- Nitrate dosing may increase nitrogen levels in the wastewater if does at a higher dosing rate.
- The dosing of nitrate convert the sulfide into sulfate and other oxidation products such as elemental sulfur and thiosulfate. The re-generation of these products at sites where nitrate is dosed results in the exposure of downstream sewer biofilms to higher level of sulfate, which enhances the growth of SRB.
- The available nitrate would be quickly consumed in sewer and during long quiescent periods, and the anaerobic conditions favorable for sulfide production would be quickly established in the system, thereby negating any positive effect achieved by nitrate dosing. In order to avoid this situation, high dosage of nitrate needs to be used.
- High VFA consumption, especially in a case where high dosage of nitrate is used, is another main concern as this would create a limitation of carbon source for downstream nutrient removal plant.
- The effectiveness and efficiency of nitrate dosing are highly sensitive to the injection locations. The selection of the injection sites and the determination of the dosage profiles could be a difficult task, particularly for a large, complex networks.
- Excessive cost in sewers with long HRT.

Further information can be obtained as follows:

- Final Report - ARC Linkage Project on Sewer Biotransformation
- Paper: Sulfur transformation in rising main sewers receiving nitrate dosage by Jiang et al. (2009)

1.8 Case studies