1 Magnesium Hydroxide

1.1 Mechanism

Magnesium hydroxide raises the wastewater pH to a level above 9.0 and thus prevents the transfer of hydrogen sulfide from liquid to gas phase. As the sewer odour and corrosion problems are directly related to the gas phase hydrogen sulfide concentration, the lower gas phase H_2S concentration prevents the occurrence of the problems.

1.1.1 Hydrogen Sulfide Equilibrium

Dissolved sulfide is present in sewage primarily in three forms, the molecular hydrogen sulfide (H_2S_{aq}), bisulfide (HS^-), and sulfide (S^{2-}) with the exact fractionation depending upon the sewage pH.

$$H_2S_{aq} \rightleftharpoons HS^- + H^+ \rightleftharpoons S^{2-} + 2H^+$$

where Ka1 and Ka2 are the equilibrium constants with the values of 7.0 and 13.0, respectively.

At neutral pH, H_2S_{aq} and HS exist in similar proportions. Shift of pH towards acidic range increases the proportion of H_2S_{aq}, while that towards the alkaline range increases the proportion of HS^-. The odor and corrosion problems are directly related to the concentration of H_2S in the gas phase, which is the result of the liquid-gas transfer of dissolved H_2S_{aq}. The rate of hydrogen sulfide transfer in mg/L.h is given by:

$$\frac{d[H_2S]}{dt} = -k_L a_{H_2S} \cdot \left([H_2S_{aq}] - \frac{[H_2S_g]}{H_{H_2S}} \right)$$

where $k_L a_{H_2S}$ is the mass transfer coefficient in 1/h, $[H_2S_{aq}]$ is the aqueous phase H_2S concentration in mg/L, $[H_2S_g]$ is the gas phase H_2S concentration in mg/L, and H_{H_2S} is the dimensionless Henry's constant. Since the rate of transfer depends upon the concentration of H_2S_{aq}, wastewater pH plays an important role in the transfer of H_2S from liquid to gas, and thus greatly influences the extent of odor and corrosion problems. The dosing of magnesium hydroxide could raise the pH to about 9.0-9.5 thereby greatly reducing the gas phase H_2S concentration.

1.1.2 Effects of Magnesium Hydroxide

The dosing of magnesium hydroxide affects the sewers in the following ways:

1. By increasing the wastewater pH, the transfer of H_2S from liquid to gas phase is prevented.
2. The activity of biofilm is inhibited under the elevated pH conditions, thus reducing the overall sulfide production.
3. There is an increase in the wastewater alkalinity.

Further information can be obtained as follows:

- Effects of long-term pH elevation
  - Paper: Effects of long-term pH elevation on the sulfate-reducing and methanogenic activities of anaerobic sewer biofilms by Gutierrez et al. (2009)

1.2 Magnesium hydroxide dosing to sewers

Magnesium hydroxide dosing is done directly into a flow stream. The dosing location could be a sewer manhole, pump station or rising main. The maximum pH that could be achieved by doing magnesium hydroxide depends upon the buffering capacity of the wastewater. In general, pH up to 9.5 could be achieved. Since the magnesium hydroxide has got limited solubility in water, excess amount of the chemical remains in solution in the solid form. Any decrease in pH due to the production of acid as wastewater flows in sewer pipe will result in the release of the solid in the form of Mg^{2+} and OH^{-}, thereby increasing the pH to the maximum level.

1.3 Dosing arrangement and typical dosing rates

As the magnesium hydroxide increases the pH by neutralizing the positive charges in the wastewater, the amount of magnesium hydroxide needed to be dosed depends upon the buffering capacity of the wastewater, which in general is the function of wastewater carbonate/bicarbonate, phosphate, ammonia, VFA, dissolved sulfide and cation/anion concentration. Highly buffered wastewater require higher magnesium hydroxide dosage to reach the maximum pH and vice versa.

Typical dosing rate of magnesium hydroxide ranges between 47.9 and 156.6 kg $Mg(OH)_2$ per ML of wastewater.

Although magnesium hydroxide could be dosed at the discharge point, it is beneficial to dose $Mg(OH)_2$ at an upstream location. This controls sulfide and methane emissions in the entire sewer pipe, with reduced chemical consumption. It also increases the availability of organic carbon for the downstream biological nutrient removal due to reduced consumption of organic carbon for methane formation.

Further information can be obtained as follows:

- Dosing arrangements
  - Dosing Control of Magnesium Hydroxide in Sewers
- Typical dosing rate
  - Paper: Chemical dosing for sulfide control in Australia: An industry survey by Ganigue et al. (2011)

1.4 Cost of magnesium hydroxide dosing

Magnesium hydroxide dosing requires storage facility for the chemical and the dosing equipments. The estimated cost of magnesium hydroxide dosing is $48.7 - $159.3/ML depending upon the buffering capacity of wastewater, HRT in the sewer, the target pH level and unit cost of chemical.

Further information can be obtained as follows:

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

1.5 Impacts on WWTP

The dosing of magnesium hydroxide produces elevated pH levels of up to 8.5, which will not have any significant adverse effects on the STP performance and may in fact improve biological N removal in STP, which have low alkalinity or low pH and may replace the need for lime dosing at some plants. However, MHL dosing may result in the formation of struvite ($MgNH_4PO_4.6H_2O$), which may cause problems due to its precipitation in pipes. The precipitation of struvite is controlled by a combination of factors, such as thermodynamics of liquid-solid equilibrium, phenomena of mass transfer between solid and liquid phases, kinetics of reactions, and several physiochemical parameters; hence, the prediction of struvite precipitation is complex. For simplicity, the precipitation of struvite can be considered to occur when the product of activities of magnesium, ammonium and phosphate ions exceeds the thermodynamic solubility product (Ksp) of struvite. With typical levels of ammonia (~50 mgN/L) and phosphate (~7 mgP/L) in domestic wastewater, struvite precipitation is likely to occur at pH above 9 when magnesium hydroxide is dosed in excess. However, the amount of struvite is not expected to be significant as small changes in concentration of NH^{4+} and PO_4^{3-} will result in the product of activities being less than the solubility product.

Further information can be obtained as follows:

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

1.6 Case studies

- Sulfide control using MHL dosing in Noosa
- Sulfide control using MHL in Yadina