1 Ferric Salts

1.1 Mechanism

Iron salts react with dissolved sulfide to form metallic sulfide precipitates thus reducing H_2S release to the sewer headspace. The addition of iron salts to sewers has been in practice since 1920s. Iron salts of chloride are added to sewer in the form of either ferrous or ferric. Depending upon the type of salt used, the following reactions occur.

The ferrous iron (Fe^{2+}) tends to react with sulfide species to form a variety of precipitant products, while ferric iron (Fe^{3+}) oxidizes sulfide species to elemental sulfur while itself being reduced to ferrous iron.

The precipitation reaction between ferrous iron and sulfide can be described as follows:

$$Fe^{2+} + S^{2-} \rightarrow FeS_{(s)} \downarrow$$

The precipitation reaction between ferric iron and sulfide can be described as follows:

$$2Fe^{3+} + S^{2-} \rightarrow 2Fe^{2+} + S^{0}$$

$$2Fe^{2+} + 2S^{2-} \rightarrow 2FeS_{(s)} \downarrow$$

The overall precipitation reactors thus becomes:

$$2Fe^{3+} + 3S^{2-} \rightarrow 2FeS_{(s)} + S^{0}$$

1.2 Effects of ferric salts dosing

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

1. By precipitating dissolved sulfide in the wastewater, it locks the sulfide into insoluble form thereby preventing its release to sewer atmosphere.
2. The dosing of ferric salt has shown considerable inhibition of sewer biofilm activity (Zhang et al., 2012). The inhibitory effect of Fe^{3+} addition on sulfate reduction and methane production by sewer biofilms is a gradual process. It takes several days for the maximum inhibition to be induced.
3. Iron salts dosage for sulfide control in sewers induces chemical phosphorus removal during wastewater treatment (Gutierrez et al., 2010).

1.3 Ferrous/Ferric dosing to sewers

Iron salts can be dosed directly into a flow stream. The dosing location could be a sewer manhole, pump station or rising main. Iron salts of sulfate or chloride are generally used. Since the hydrogen sulfide production generally increases with increased sulfate level in wastewater, especially in cases where sulfate is present at a low concentration, dosing of iron sulfate salts is not recommended.

1.4 Dosing arrangement and typical dosing rates

In order to reduce sulfide to concentrations lower than around 0.1 mg S/L with a safety factor, a molar ratio higher than around 1.3 (Fe) to 1 (S^{2-}) should be applied when ferrous salts are used, and that of 0.9 to 1 when ferric salts are applied (Firer et al., 2008).

The amount of salt required to be dosed also depends upon the pH. To achieve the same level of hydrogen sulfide in sewer, higher Fe:S ratio is required at a low pH and vise versa. However, beyond the pH of 7.5, there is very little impact of the pH.

Based on the current industry practice, iron salts are dosed at 3-47 kg Fe/ML, the dosing rate depending upon the hydrogen sulfide level in the wastewater.

Dosing of ferric chloride at an upstream location helps to reduce overall sulfide production thereby providing some savings to the cost of chemical. On the other hand, dosing of ferric at a location close to the treatment plant has got benefits of removing phosphate during the wastewater treatment without additional ferric dosing.

Further information can be obtained as follows:

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

1.5 Cost of iron dosing

Typical cost of iron salt dosing is $10.9 - $170.6/ML (the cost depends upon the hydrogen sulfide level, wastewater pH, target sulfide 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)

1.6 Impacts on WWTP

Dosing of ferric chloride resulted in hydrogen sulfide precipitation in the form of FeS precipitates, which would enter the STP. Once the FeS particles enter the STP aeration tank, FeS precipitates get oxidized to Fe^{3+} and $SO_4{}^{2-}$ in the aeration tank and the Fe^{3+} thus formed results in the precipitation of $PO_4{}^{3-}$. A primary settling tank (if part of the STP) may remove FeS with the sludge that is removed from the bottom of the tank, however it has been found that a negligible fraction of FeS particles will be retained in the primary settling tank if the $FeCl_3$ was dosed close to the STP inlet, resulting in a short contact time insufficient for FeS colloids to form large-sized particles.

The amount of ferric added to the sewer to achieve a desirable sulfide level in the sewer (below 1mg S/L) is usually sufficient to achieve an effluent P level of approximately 2.5 mgP/L in the STP effluent, which is comparable to that achieved by direct dosing of the same amount of $FeCl_3$ to the STP.

Further information can be obtained as follows:

- Paper: Iron salts dosage for sulfide control in sewers induces chemical phosphorus removal during wastewater treatment by Gutierrez et al. (2010)
- Paper: Integrated modelling of sewer system and wastewater treatment plant for investigating the impacts of chemical dosing in sewers by Sharma et al. (2012)

1.7 Case studies

- The use of iron salts to control dissolved sulfide in Los Angeles Country Sewer District's Trunk Sewers