

Experiences with iron chloride dosing to control sulfide-induced corrosion problems in sewers

Brecht Donckels*, Greet De Gueldre, Marjoleine Weemaes

Research and Product Development Division, Aquafin N.V., Belgium

Abstract:

Dosing iron salts is one way of dealing with sulfide-induced corrosion problems in sewers. By dosing iron salts such as FeCl_2 and FeCl_3 , the dissolved sulfide molecules present in the wastewater chemically react with $\text{Fe}^{++(+)}$ to form elemental sulfur (S^0) and iron sulfide (FeS). These products precipitate and thereby the amount of sulfide available for release to the sewer atmosphere decreases.

After a test phase *on-site*, this control measure was implemented in full-scale to deal with sulfide-induced corrosion problems that had been observed at a pumping station in the vicinity of Antwerp, Belgium. This contribution describes Aquafin's experiences with this control measure and elaborates on how the effectiveness was tested and evaluated prior to a full-scale application. Further, it describes how the dosage was implemented in full-scale and presents the results obtained so far. To conclude, the pros and cons of this control measure are discussed based on our experiences so far.

Keywords: hydrogen sulfide, biogenic sulfuric acid corrosion, sewer, iron chloride dosing

* Corresponding author: brecht.donckels@aquafin.be

Introduction

Aquafin was established in 1990 by the Flemish government and is responsible for the design, construction, operation and pre-financing of the supra-municipal wastewater treatment infrastructure of Flanders, which is the northern part of Belgium residing approximately six million inhabitants. Basically, this means that cities and municipalities are responsible for their own sewer systems, but their sewer networks connect to Aquafin's collector (or interceptor) sewers that transport the wastewater to the wastewater treatment plant.

Anno 2011, Aquafin's assets include 247 wastewater treatment plants, 1174 pumping stations and approximately 4735 km of collector sewers. The wastewater collection system, which covers the majority of Aquafin's assets and still expands at a rate of approximately one km per day, is the main focus of this paper. More precisely, this paper deals with the problems wastewater service providers around the world are facing that can be appointed to the presence of hydrogen sulfide in the wastewater collection system.

To introduce the terminology used in this paper, the different parts of a conventional wastewater collection system are shown schematically in Figure 1. Wastewater from the households is mainly and preferably transported through gravity sewers, but it is often not possible to reach the wastewater treatment plant in this manner. Therefore, pumping stations are needed, where the

wastewater is collected in a wet well which is equipped with level measurement instruments that monitor the amount of wastewater present. When full, the wastewater is pumped to a higher level through a force main (or pressure main or rising main) and discharged in an inspection chamber or manhole from which the wastewater continues its path through gravity sewers. This is typically repeated until eventually the wastewater arrives at the wastewater treatment plant. Needless to say that the sewer system is hardly ever a linear system, and often many sewer pipes are connected with each other to form a complex network with many branches.

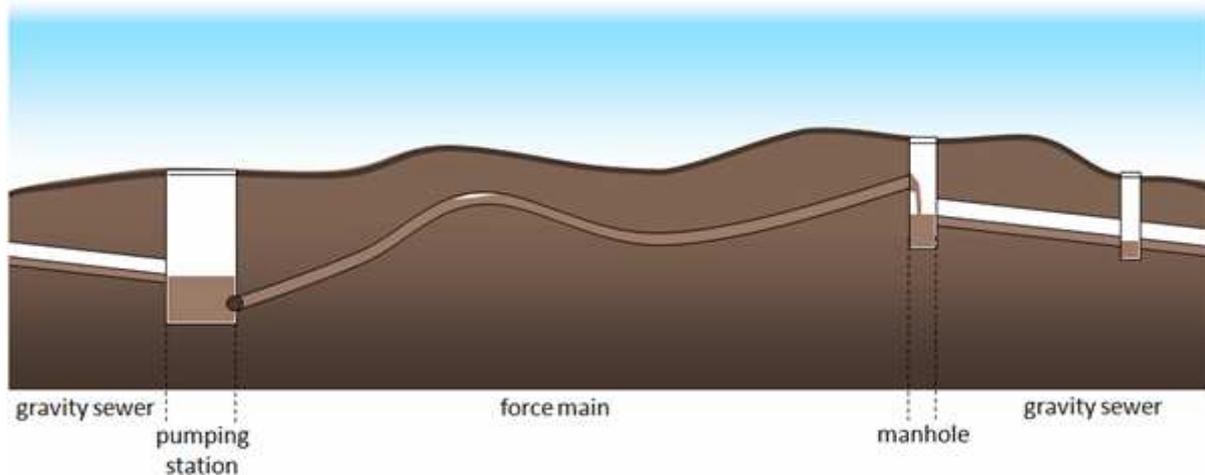


Figure 1: Schematic representation of a simplified, conventional wastewater collection system, illustrating its most common constituents.

As stated above, some problems that arise in the sewer infrastructure are caused by the presence of hydrogen sulfide (H_2S). Sulfides are formed under anaerobic conditions, which in this context can be interpreted as conditions where oxygen is absent (sewage does typically not contain nitrate). Anaerobic conditions can occur at different places in the sewer infrastructure (Figure 1 and Figure 2), such as:

- force mains;
- inverted siphons;
- gravity sewers with high filling degree;
- slow-flowing, partially filled gravity sewers;
- biofilm and sediment layers found in gravity sewers;
- wet well of pumping stations and other places where the wastewater stands still for a significant amount of time.

After being emitted to the sewer atmosphere, hydrogen sulfide will initiate a process called biogenic sulfuric acid corrosion. The concrete sewer pipes corrode and lose their mechanical strength. In addition, malodorous compounds are typically formed under the same anaerobic conditions as hydrogen sulfide and the latter thus contributes to odor nuisance. In this paper, however, only corrosion problems are dealt with.

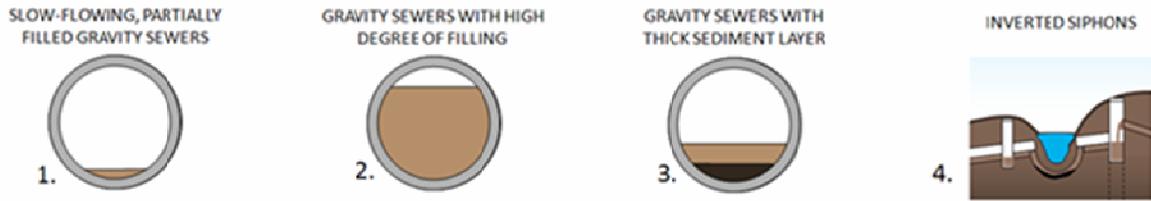


Figure 2: Situations that may occur in the sewer system where hydrogen sulfide can be accumulate (other than force mains).

Several technologies are being used by the wastewater industry to minimize the adverse effect of hydrogen sulfide formed in sewer systems (see, for instance, ASCE (1989), Hvitved-Jacobsen (2002), and Zhang *et al.* (2009) for an overview). Common sulfide control measures include the injection of air or pure oxygen in the force main or the dosage of nitrate salts in order to prevent sulfide formation. Another approach to the problem is the addition of $Mg(OH)_2$ to elevate pH, thereby minimizing the transfer of molecular H_2S to the gas phase. In this paper, the addition of iron salts will be discussed – more precisely the addition of ferrous and ferric chloride ($FeCl_2$ and $FeCl_3$).

This paper is organized as follows: in the following chapter, the theoretical background with regard to the processes that take place when iron chloride is dosed into sulfide-rich wastewater will be described. As this paper focuses on our experiences in practice, the case study where this control measure is applied is then briefly presented and the results obtained during a test phase are discussed. Also the full-scale application and some preliminary results are presented and finally, the conclusions are summarized.

THEORETICAL BACKGROUND

When dosing metal salts to sulfide-rich wastewater, one basically aims at chemical precipitation of the dissolved sulfides. Obviously, this prevents the release of sulfides from the wastewater and the process of biogenic sulfuric acid corrosion can thus not initiate. The most common metal salts that are used to prevent the adverse effects of high sulfide concentrations in the sewer system are Fe(II) and Fe(III), either as sulfate or chloride (Hvitved-Jacobsen, 2002). Note that Fe(II) and Fe(III) salts are called ferrous and ferric salts, respectively.

When ferrous or ferric salts are added to sulfide-rich wastewater, they dissociate and one or both of the following reactions will, at least in theory, take place:



Looking at the reaction stoichiometry, one can see that Fe(II) can remove sulfide by precipitation as ferrous sulfide (FeS) according to Eq. (2), whereas Fe(III) can remove sulfide by oxidizing it chemically to elemental sulfur while being reduced to Fe(II), which can subsequently produce FeS (both Eq. (1) and Eq. (2)). One can see that according to these stoichiometric reactions, 1 mole of Fe(III) will react with 1.5 mole of hydrogen sulfide, whereas this is only 1 mole of hydrogen sulfide for each mole of Fe(II). However, this is theory and does not take into account the fact that Fe(II) and Fe(III) may also react with other components that are present in the wastewater (Gutierrez *et al.*, 2010).

Literature on the subject is not always clear about the actual yield that is observed in practical applications and it appears that the yield is highly dependent on site-specific parameters. Zhang *et al.* (2010) have reported that approximately 0.7 mole of Fe(II) was required to precipitate sulfide formed from the reduction of one mole of sulfate, which is significantly lower than the ratio expected from reaction stoichiometry (that is, a molar ratio of 1:1). Similar yields were observed for Fe(III) (personal communication Prof. Zhiguo Yuan), while Nielsen *et al.* (2005) report a stoichiometric yield of approximately 1 mole H₂S-S/mole Fe(III). Whether ferrous or ferric iron is most effective in controlling the dissolved sulfide concentration is not clear from literature either (Nielsen *et al.*, 2005).

Wert *et al.* (2007) have investigated the iron chloride dosage for the mitigation of sulfide concentration in biogas and observed a dosage gain when injecting ferric chloride into anaerobic environments, whereas the presence of oxygen appeared to improve the performance of ferrous chloride addition (although either form is said to be appropriate for aerobic locations). Other field studies showed that despite the very low solubility of iron sulfide, complete control of dissolved sulfide is difficult and iron salts must be added in excess to obtain adequate control. The key parameter that controls effective injection is adequate mixing (Wert *et al.*, 2007). In addition, the pH of the wastewater is preferably kept above 6.5 to avoid instability of the FeS formed.

Apart from stoichiometry, also reaction kinetics are important (especially for the case study dealt with in this paper, see further). Indeed, the added iron salts are expected to have reacted with the dissolved sulfides present in the wastewater, before they are emitted to the sewer atmosphere at points of turbulence. The precipitation reaction is fast, but it is unclear whether this is also the case for the oxidation reaction. It is clear that adequate mixing is very relevant in this respect, as it may reduce the required reaction time significantly.

RESULTS AND DISCUSSION

Site description

During the inspection of a collector sewer of approximately five years old, severe damage to the concrete pipe was observed that could be appointed to biogenic sulfuric acid corrosion. Since an inspection held one year earlier did not reveal significant corrosion, the loss of wall thickness occurred in a time span of maximum two years and the corrosion rate could thus be considered as fairly high.

Since the collector sewer (with a diameter of 1600 mm and an original wall thickness of 13.5 cm) transports the wastewater of a large part of a Flemish city (±250.000 IE), it can be considered as strategically important and the situation was dealt with immediately.

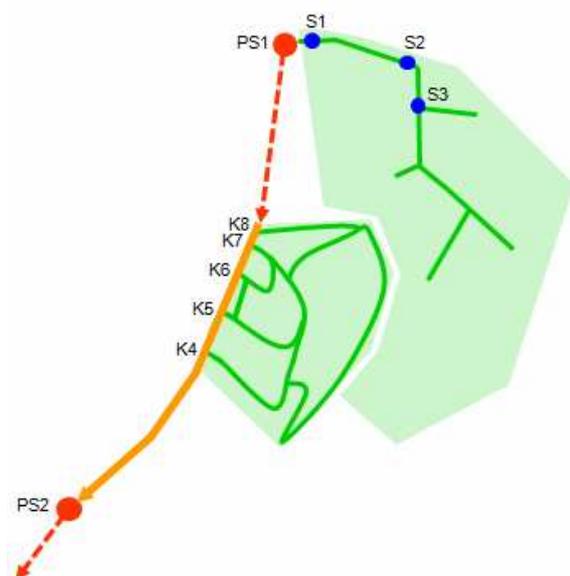


Figure 3: Schematic representation of the case study discussed in this paper.

The collector (represented by the orange arrow in Figure 3) receives wastewater from a force main (the dashed red arrow) which originates at pumping station PS1, that was only operational for two years at the time of inspection. By taking this pumping station in operation, the deterioration rate seems to have increased significantly and the main contribution to the corrosion problems in the collector has to be attributed to this sewer stretch.

However, contrary to what was expected intuitively, the underlying cause was not sulfide formation in the force main, but in three old siphons upstream of the pumping station. These siphons were built in the 1930's and because of their dimensions, the flow velocity is (too) low. Although it could not be observed visually, a significant amount of sediments and debris is expected to have accumulated over the years. In this sediment layer, sulfides are likely to be formed and measurements have confirmed that the sulfide concentration increases significantly as the sewage passes a siphon (results not shown).

The sulfides formed in the siphons upstream of pumping station PS1 can thus explain (at least part of) the corrosion problems observed in the collector, but also the concrete walls of the wet well of the pumping station show signs of corrosion (Figure 4) and control measures are required in order not to compromise the pumping station. On the long term, the siphons will be bypassed with new ones that are dimensioned properly, thereby avoiding long retention times and sedimentation. However, on the short term, dosing iron salts was believed to be the most appropriate measure to control the corrosion taking place in the wet well until the long term solution is deployed (within a few years).



Figure 4: Corrosion of the concrete walls of the wet well of pumping station PS1 in November 2009 (left and middle) and April 2011 (right).

Test phase

From the moment that the decision was made to dose iron salts to protect the pumping station against further sulfide-induced corrosion, it was decided to include a test phase. This not only because the full-scale application of iron chloride dosing required a significant investment, but also because it was unclear whether the dosage would be effective. Indeed, although the dosage of iron salts was suggested as the most appropriate control measure for this specific situation by several independent consultants, one could not guarantee that the reaction time of a few minutes would be sufficient to reduce the sulfide concentration significantly.

During the test phase, tests were performed from 1 m³ containers (Figure 5), because Flemish environmental legislation did not allow us to store a larger amount of iron chloride on site. Because we primarily wanted to investigate the effectiveness of the dosage, iron chloride was dosed each other day while the sulfide concentration (gas phase) in the wet well was continuously monitored, as well as the temperature and pH of the wastewater.



Figure 5: During the test phase, iron chloride was dosed from 1 m³ containers.

As stated above, literature is unclear about the relative effectiveness (in practice) of ferric and ferrous chloride and, therefore, both products were considered in the test phase. The measurements collected during the entire test phase are shown in Figure 6, and the periods in which ferrous and ferric chloride were dosed are indicated by the light and dark grey bars, respectively.

From the results depicted in Figure 6, it is difficult to conclude whether dosage iron chloride is effective or not; nor whether there is a difference in effectiveness between both products. However, after looking at the measured sulfide concentrations in a different way (Vollertsen *et al.*, 2005), some conclusions can be drawn. For this, the original data set was split into three data subsets: (1) without iron chloride dosing, (2) with ferrous chloride dosing and (3) with ferric chloride dosing. Then, cumulative probability distributions were calculated for each data subset, representing the time (in percentage) during which the measured sulfide concentration was lower than a given value (Figure 7).

Looking at the results from Figure 7, one can clearly see that iron chloride dosing is effective for both FeCl₂ and FeCl₃. Indeed, the green line is closer to the y-axis than the red line, indicating that the overall concentrations were lower when iron chloride was added to the wastewater. For example, in the period when FeCl₃ was tested, the sulfide concentration was below 10 ppm for approximately 60% of the time, while this was only 40% when no FeCl₃ was dosed (that is, 20% less). The measurements also suggest that FeCl₃ was slightly more effective, compared to FeCl₂.

Still, it is clear that there is/was room for improvement. Although Gutierrez *et al.* (2010) and others have suggested to dose iron salts upstream in the sewer network, practical limitations did not allow this for the current project and the dosing had to be implemented on the terrain of the pumping station. As a consequence, the time between the point of injection and the point of turbulence (where the wastewater falls into the wet well and where the dissolved sulfides are emitted) is limited. The reaction between Fe(II) and/or Fe(III) and the dissolved sulfides must have proceeded as much as possible in this period of time and, consequently, a better mixing of the added iron chloride may be very beneficial for the effectiveness and efficiency of the dosing.

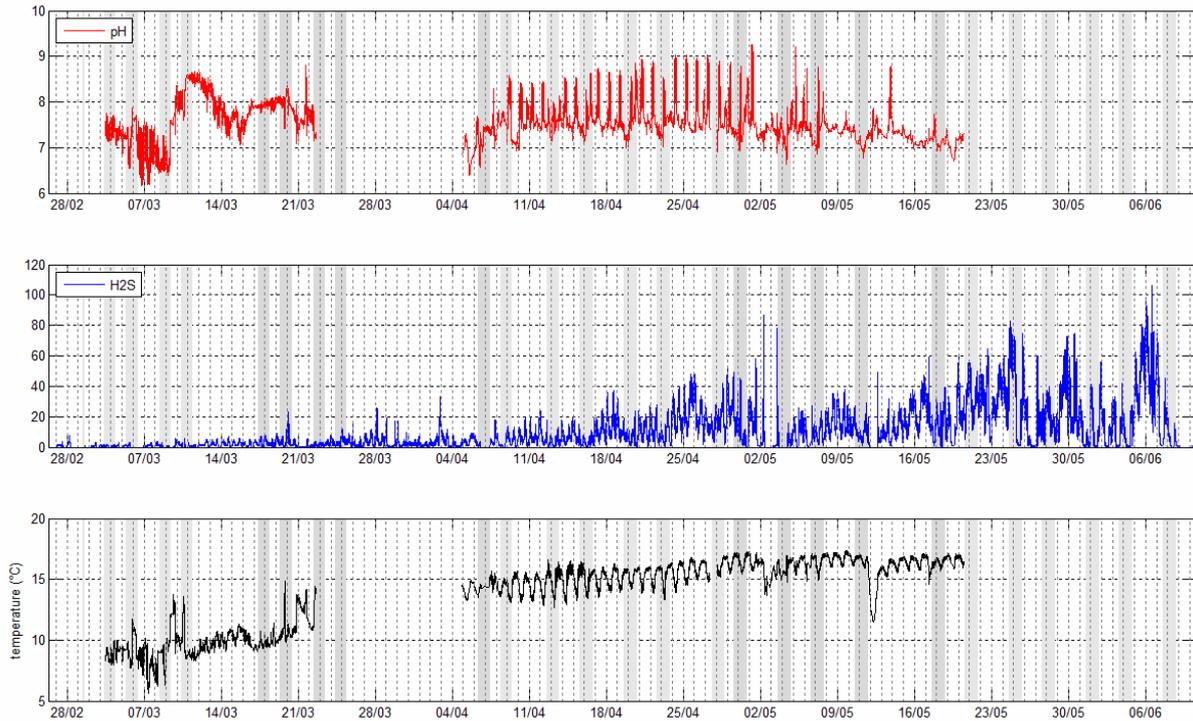


Figure 6: Measured profiles of pH, H₂S concentration in the gas phase of the wet well (in ppm) and temperature of the wastewater (in °C). The light gray bars indicate periods where FeCl₂ was dosed, and the dark gray bars depict periods where FeCl₃ was dosed. Note that for pH and temperature, some data is missing.

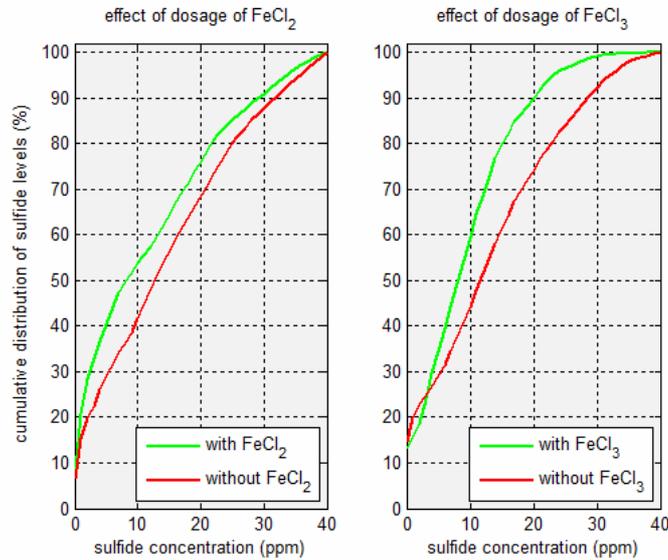


Figure 7: Cumulative probability distributions of the measured sulfide concentration in the gas phase (ppm) for the periods during which iron chloride was (green) and was not (red) dosed. The results for ferrous chloride are shown in the left graph, whereas the results for ferric chloride are shown on the right graph.

Full-scale application

Full-scale application of the iron chloride dosage started in October 2010 and ferric chloride was preferred over ferrous chloride. The latter was decided based on the results of the test phase, but also on cost-related considerations. Full-scale test with ferrous chloride are however not excluded.

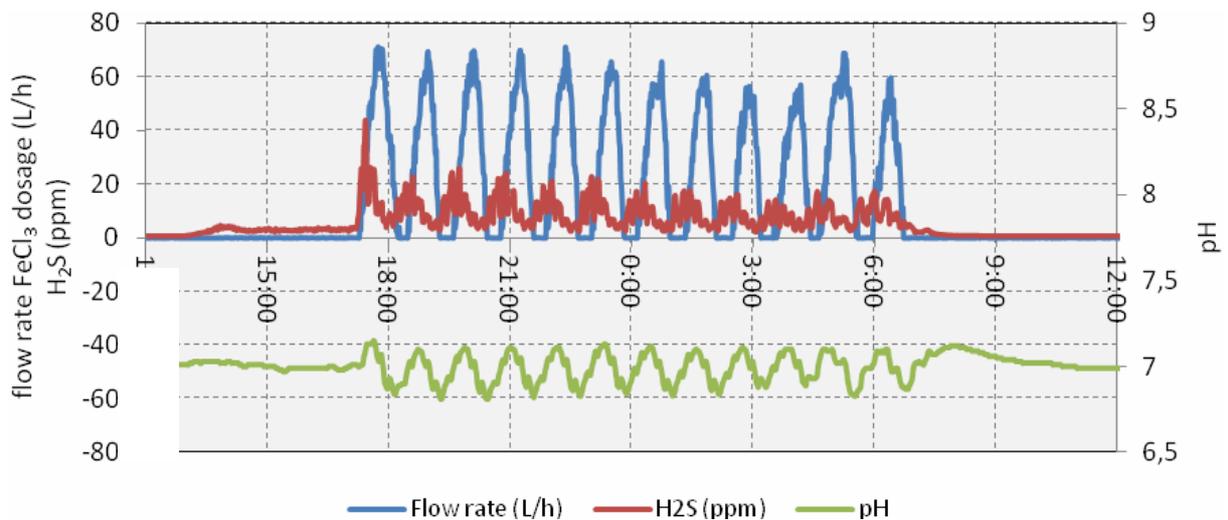


Figure 8: Data measured on the 24th of November, clearly showing that the dosage of FeCl₃ is effective in significantly reducing the sulfide concentrations in the wet well of the pumping station.

The results obtained from February till April 2011 (Figure 9) show that the sulfide concentration were below 10 ppm for most of the time, but also show that more sulfide is produced as temperatures increase. The amount of product dosed is controlled and the underlying control algorithm (developed in-house) is based on a continuous measurement of the sulfide concentrations in the wet well and the pH of the wastewater. As stated previously, the pH of the wastewater may not become too low in order to maintain the insolubility of the particulate FeS molecules, which is incorporated in the control algorithm.

The measurements depicted in Figure 8 illustrate the effectiveness of the dosage (and its control). Indeed, during this period the pH threshold was set at a value of 7.0, which is in fact a bit too high. As the pH of the wastewater was only slightly higher than 7.0, the pH dropped rapidly when ferric chloride was added and the dosage rate was reduced. This clearly resulted in an increase in the measured sulfide concentration, illustrating that that a significant fraction of the dissolved sulfides do react with added iron salts.

As the temperatures will increase in the warmer months, the measurements will be followed with great interest and the true potential of iron chloride dosage for the present case study will become apparent. As stated above, the injection point had to be located close to the pumping station (approximately 30 m) so the reaction time is limited. If sulfide levels cannot be kept below 10 ppm in the warmer months, a more adequate mixing would be the first thing to try in order to increase the effectiveness of the dosage.

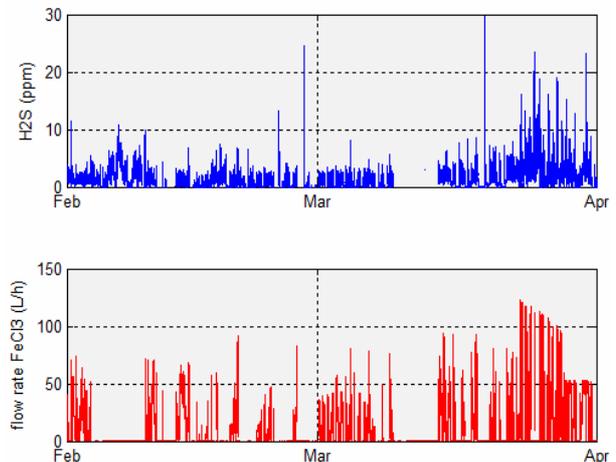


Figure 9: Hydrogen sulfide concentration (in ppm) measured in the wet well of the pumping station (upper graph) and the rate at which ferric chloride (in L/h) is added to the wastewater (lower graph).

Knowledge gaps

Although the dosage of iron salts is generally referred to as a proven technology, some questions remain partly unanswered:

- Knowledge on the rate at which the precipitation and/or oxidation reactions proceed is incomplete, although this is important for practical applications as this determines the optimal injection point. For applications where the sulfide formation in the force main is the underlying cause, this may not as be crucial/problematic as for applications like the one described above.
- It is clear that the operational costs are driven by the molar ratio at which the sulfides react with the added iron salts. Literature and practical experience both state that the yields observed in practice are significantly less than expected from theory, but it remains unclear to what extent this yield depends on wastewater quality parameters that are often site-specific (COD, pH, temperature, buffer capacity and ORP levels). In other words, operational costs are difficult to predict prior to implementation.
- It is unclear what will happen with the products of the chemical precipitation. Probably, the precipitates will not accumulate in the sewer as the particles are too small to settle, and they will be transported to the wastewater treatment plant (WWTP). If so, to what extent will this dosage of iron salts lead to an increased cost for sludge treatment. If significant, this has to be added to the operational cost of this sulfide control measure.
- Hvitved-Jacobsen (2002) and Gutierrez *et al.* (2008) have reported that the FeS particles are oxidized in the aeration tank of the WWTP and will aid in the chemical removal of phosphorous, leading to a lower net operational cost of the dosage. This was observed on lab-scale (Gutierrez *et al.*,2008), but to the author's knowledge, this has not been investigated in full-scale application. It is therefore unclear to what extent this can be taken into account.
- In this case study, the time between point of injection and point of turbulence was short, which made it practically feasible to control the dosage aiming at a reduced operational cost. Such control may not be possible when iron chloride is added further upstream, as suggested by Gutierrez *et al.* (2008).

CONCLUSIONS

The presence of high concentrations of hydrogen sulfide in the wastewater may result in serious corrosion problems, especially at locations with high turbulence. The latter is typically observed after force mains with high retention times, but biogenic sulfuric acid corrosion may also occur when sulfide-rich wastewater arrives at a pumping station. Dosing iron salts, such as FeCl₂ and FeCl₃, is one of the approaches to deal with high sulfide concentrations. Both products were tested and both were shown to be effective, in the sense that they resulted in a decrease of the sulfide concentration in the wet well atmosphere and thus in a decreased corrosion rate. A slightly better performance was observed for FeCl₃. Full-scale application confirmed that dosing iron chloride makes sense and during the cold winter months it was possible to maintain low sulfide concentrations (< 10 ppm) in the wet well of the pumping station, thereby reducing the corrosion rate.

REFERENCES

- Gold Coast Water (2007). *Model based management for hydrogen sulfide in sewers*. Research Report, February 2007.
- Gutierrez O., Park D., Sharma K.R. and Yuan Z. (2005). *Iron salts dosage for sulfide control in sewers induces chemical phosphorus removal during wastewater treatment*. *Water Research*, **44**(11), 3467-3475.
- Hvitved-Jacobsen T. (2002). *Sewer processes – Microbial and chemical process engineering of sewer networks*. CRC Press, pp. 237. ISBN 1-56676-926-4.
- Nielsen A.H., Lens P., Vollertsen J. and Hvitved-Jacobsen T. (2005). *Sulfide-iron interactions in domestic wastewater from a gravity sewer*. *Water Research*, **39**(12), 2747-2755.
- Padival A.N., Kimbell W.A. and Redner J.A. (1995). *Use of iron salts to control dissolved sulfide in trunk sewers*. *Journal of Environmental Engineering*, **121**(11), 824-830.
- Vollertsen J., Nielsen A.H., Yang W. and Hvitved-Jacobsen T. (2005). *Effects of in-sewer processes: a stochastic model approach*. *Water, Science and Technology*, **52**(3):171-180.
- Wert W., Patel D., Mellin J. and Garza F. (2007). *Ferric/ferrous chloride injection optimization as demonstrated by regional case studies*. *Water Practice*, **1**(1), 1-13.
- Zhang L., De Schryver P., De Gusseme B., De Muynck W., Boon N. and Verstraete W. (2008). *Chemical and biological technologies for hydrogen sulfide emission control in sewer systems: A review*. *Water Research*, **42**(1-2):1-12.
- Zhang L., Keller J. and Yuan Z. (2009). *Inhibition of sulfate-reducing and methanogenic activities of anaerobic sewer biofilms by ferric iron dosing*. *Water Research*, **43**(1-2):4123-4132.
- Zhang L., Keller J. and Yuan Z. (2010). *Ferrous salt demand for sulfide control in rising main sewers: tests on a laboratory-scale sewer system*. *Journal of Environmental Engineering*, **136**(10): 1180-1188.