Centre for Infrastructure Engineering

SCHOOL OF COMPUTING, ENGINEERING AND MATHEMATICS

EVALUATING SEWER CORROSION CONTROL OPTIONS USING A NOVEL LABORATORY SCALE SEWER SYSTEM

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Declaration

To the best of my knowledge and belief, this thesis contains no material previously published by any other person except where due acknowledgment has been made.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

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Abstract

Hydrogen sulfide (H_2S) generation in sewer systems presents a significant cost to public due to metal and concrete corrosion and destruction of the asset and is responsible for obnoxious odour and potential toxicity.

Several methods are adopted to control the corrosion. Most popular methods are dosing chemicals either to bind the H_2S or to adjust pH to higher values to convert H_2S to a form that will prevent the emission to air. Effectiveness and cost of these methods vary from researcher to researcher. Mainly due to the poor access system, fundamentals behind the effectiveness are not clear. Fundamentals are not properly understood because simulating the sewer system, especially partial flow sewer, is challenging due to exposure to atmosphere and a high flow velocity and hence there was no single laboratory model that was available to simulate conditions.

The main objective of this research is:

- To develop a laboratory testing system capable of generating H_2S in similar conditions to a real sewer system
- To evaluate various control measures of sulfate reduction in the sewer system
- To understand the mechanism of H_2S generation and control
- Formulate a more cost-effective H_2S control method
- Development of the model

To achieve the main objectives, a combination of two traditionally used methods –pH control using lime and ferrous chloride addition- were tested. Synthetic wastewater was fed into the reactor. Produced hydrogen sulfide concentrations were measured using the colorimetric method. Reduction of H_2S in the gas phase was monitored with the concentration of dissolved oxygen in the liquid phase. The comparison of the existing hydrogen sulfide control methods with the tested combined method of pH adjustment and ferrous chloride dosing exhibited important benefits of the new method. This method was found to be more efficient and cost effective. Due to sludge reduction and chemical reduction, the treatment process (sludge treatment process) will be much easier in the downstream.

The addition of ferrous chloride at higher pH reduced the gas phase H_2S concentration even further as did the presence of oxygen. The discrepancy between actual H_2S gas phase measurements and the theoretical gas phase values was identified. Silver nitrate titration using a silver electrode was used to identify the final products of the reactions. To further identify the sulphur species, a model using stoichiometric coefficients was developed and tested under various experimental conditions. It was noted, that SO_4^{2-}, $S_2O_3^{2-}$, S_o and disulfide were the major species formed in the sewer with the variation of DO level and H_2S level in the liquid phase. Formation of disulfide is advantageous, as it requires low DO level which may already exist in gravity sewers. In addition, the disulfide can not be converted back to gaseous form or processed by microbes into H_2S.

The findings of this work were used for the design of the proposed experimental and theoretical work. The data produced in the experimental work was used to develop a process model of the combined oxidation of H_2S and reduction of its concentration in the sewer headspace. Such a model can be used to optimize H_2S in a gravity sewer system, achieving the required gas concentration reduction at a minimum cost.

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Chapter 1 : Introduction

1.1 Background

The production of hydrogen sulfide (H_2S) in sewer systems results in odour problems and corrosion of sewer infrastructure (Nielsen, Asbjørn Haaning et al. 2008; Zhang, Lehua et al. 2008) (Boon 1995). Concrete sewer pipes are subjected to hydrogen sulfide atmosphere in the headspace. In the presence of condensed water drops and oxygen, hydrogen sulfide is oxidized to sulphuric acid, which over time converts calcium from the cement to calcium sulfate, resulting in severe loss of structural strength. In severe cases, this can lead to structural failure and the collapse of the sewer infrastructure within ten to twenty years. It costs water utilities billions of dollars each year (Brongers 2002). This phenomenon is particularly widespread in countries with a warm climate. A major mechanism of H_2S generation is the action of sulfur reducing bacteria (SRB) (Figure 1.1). The SRB use sulfate to oxidize organic carbon in sewer generating energy and reducing sulfate to sulfide. The SRB colonize the anaerobic regions of the pipe biofilm (Baumgartner et al. 2006; Nielsen, PH, Raunkjær & Hvitved-Jacobsen 1998; Norsker, Nielsen & Hvitved-Jacobsen 1995). The produced dissolved sulfide is mixed in the wastewater liquid phase due to prevailing hydraulic condition. A part of the H_2S from the aqueous phase is emitted into the headspace of the sewer. There, in the presence of oxygen and moisture, sulfur-oxidizing bacteria convert H_2S to sulfuric acid. The sulfuric acid reacts with the binder in the concrete producing ettringite and gypsum and causes sewer corrosion(Mori et al. 1992; Roberts et al. 2002).

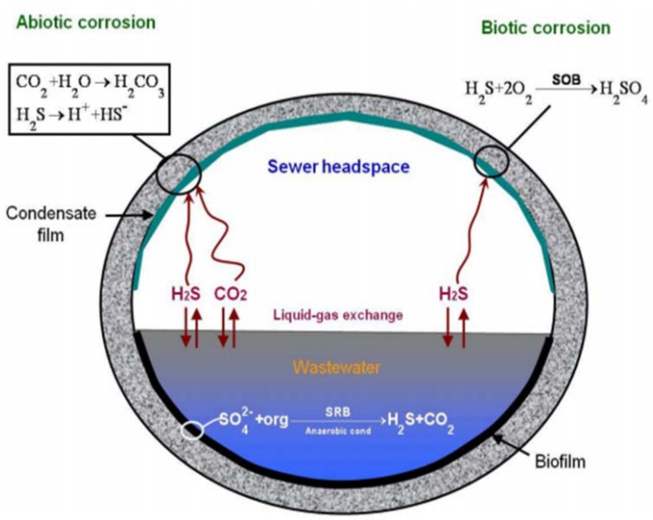

Figure 1.1: Sewer corrosion reaction gravity sewer pipe

1.2 Major challenges

The concentration of H_2S in wastewater is determined by production rates in the liquid phase, emissions rates into the headspace and oxidation of H_2S by oxygen present in the headspace entering through the leakages in sewer system infrastructure. The rate of sulfide production is influenced by factors like pH, temperature, nutrients, hydraulic retention time, pipe surface, and biofilm (Delgado et al. 1999). As SRB are slow growers, they are mostly abundant in biofilms. Biofilms are always submerged in flowing water containing high biochemical oxygen demand (BOD) and a limited amount of oxygen which provides an ideal condition for H_2S production (Firer, Friedler & Lahav 2008). Emission of H_2S into the gas phase is widely reported to be mainly controlled by the total dissolved sulfide concentration in the form of associated molecule of H_2S. Hence, water utilities use chemicals to reduce dissolved H_2S in the liquid phase of the sewer. The introduced chemical should be user and environmentally friendly, cost effective to use and must not interfere with downstream wastewater treatment processes.

In the liquid phase of the sewer, the pH determines what proportion of sulfide spices is in the form of H_2S, and that concentration determines equilibrium concentration of H_2S in the gas phase. If the pH increases above 9.5, the escape to the headspace can be prevented , as most sulfide spices are in the ionic forms of H_2S (HS^- and S^{2-}).The ionic forms do not enter gas phase.

1.3 Research Objectives

The $FeCl_2/FeCl_3$ dosing is the most popular method of corrosion control. However, the addition of metal salts (such as $FeCl_2/FeCl_3$) increases the amount of produced sludge, alters the characteristics and makes the sludge difficult to digest anaerobically. Also, the fundamental behind various reactions involved during dosing of $FeCl_2/FeCl_3$ are not clear (Firer, Friedler & Lahav 2008). It is, therefore, important to reduce the amount of dosed chemical and develop understanding of fundamentals. Such reduction not only reduces the cost of sludge disposal, but also the chemical cost. One good option is to combine control methods ($FeCl_2/FeCl_3$ dosing, adjusting the pH and using available O_2 in the sewer) to effectively reduce the cost and increase the sludge treatability. Such fine control needs an investigation in a controlled environment. A reliable system, where such an investigation can be carried out, is not available.

Development of laboratory scale sewer system, simulating the actual sewer line was very important to investigate sewer corrosion control options. So developing a laboratory testing system with the capability to generate H_2S under similar conditions to a real sewer system was one of the major objectives of the research.

After achieving similar conditions in laboratory scale sewer system as an actual sewer line, various sewer corrosion controlling measures and as well as combined controlling methods were evaluated according to the effectiveness and the cost efficiency.

The mechanism behind the identified effective controlling method was needed to understand for the proper evaluation and reporting. Development of the model will be useful for the implementation of the new technology to control corrosion in a real sewer. Therefore, a model was developed.

1.4 Scope of Study

To achieve the objectives, a laboratory scale reactor system was designed and operated by simulating an actual sewer line. In all cases synthetic wastewater was fed. One widely adopted controlling method was tested in the laboratory scale reactor system. Wastewater paramters such as H_2S (both in gas and liquid phases), sulphate , DOC, pH and DO were monitored as the main parameters to evaluate the performance of the proposed method. Additionally, a series of batch experiments was conducted to explain the fundamentals of the observations and to validate the outcomes. Moreover, using the experimental results, a mathematical model was also developed. Due to various reasons, actual wastewater was not used in the reactor during this part of the study.

Chapter 2 : Literature Review

2.1 Governing factors for the hydrogen sulfide formation and the emission

2.1.1 Sulphate-reducing bacteria (SRB)

For domestic wastewater, the key source of sulfur is sulfate (SO_4^{-2}) in the range of 40–200 mgL^{-1}. Aluminum sulfate addition in water treatment as coagulant contributes substantially to the sulfate level in the sewer (Araújo et al. 2000). The SRB are microorganisms which use sulfate as an electron acceptor (oxidant) in the degradation of organic compounds and produce sulfide (Muyzer & Stams 2008). In the sewer line, SRB is attached to the wall biofilm to access both the oxidant - sulfate and organic compounds. Area of the anaerobic biofilm and the thickness of the biofilm are two of the main factors in determining the rate of sulfate reduction(Hvitved-Jacobsen, Vollertsen & Nielsen 2013) and consequently hydrogen sulfide production.

2.1.2 Biodegradable organic matter (BOM)

In the process of dissolved sulfide production in the anaerobic condition, BOM acts as an electron donor. The BOM concentration is, therefore, one of the major factors for the SRB activity. It has been identified that high concentrations of BOM in high-strength wastewater (especially industrial wastewater) increases the production of dissolved sulfide than the residential wastewater (Hvitved-Jacobsen, Vollertsen & Nielsen 2013). However, the control BOM is practically impossible as the transport of the BOM to the treatment plant is the main purpose of a sewer system. The production of H_2S from acetate (representing the BOM) and sulfate can be written as follows:

$$CH_3COOH + SO_4^{2-} \rightarrow S^{2-} + 2CO_2 + 2H_2O \qquad [1]$$

From the above equation it can be seen that while sulfate provides oxygen to BOM, BOM provides hydrogen to H_2S.

Ultimately, sulfate can oxidize BOM to carbon dioxide. In practice in the sewer, there is a large excess of BOM in comparison to sulfate resulting in an incomplete mineralization of carbon. Rather oxygen content of BOM molecules is increased converting alcohol group to aldehydes (-C=O H), ketones (-CO-) or to organic acid groups of -COOH.

2.1.3 The pH

Sulfide can exist in water as H_2S (aq), HS^{2-} (aq) and S^{2-} (aq); the relative concentrations vary according to the pH (Lahav, Sagiv & Friedler 2006). However, sulfide emits only as H_2S, since ionic form (HS^{-} (aq) and S^{2-} (aq)) cannot pass through the air–water interface. The concentration of S^{2-}(aq) is negligible at a pH below 10.5, and the pH of a sewer is about 7.6. Therefore, total concentrations of H_2S (aq) and HS^{-}(aq) is measured as the total sulfide in the sewer water samples. The emission rate of H_2S from the liquid to the gas phase is proportional to the H_2S (aq) concentration and hydrodynamic conditions at the liquid gas interphase. The distribution of total dissolved sulfide between H_2S (aq) and HS^{-} is determined by pH, according to the following equilibrium relationship:

$$H_2S \leftrightarrow H^+ + HS^- \leftrightarrow S^{2-} + 2H^+ \qquad [2]$$

According to Figure 2.1, it is clear that H_2S is the main compound at a lower pH and when the pH is increased above 8, HS^{-} is dominant and when the pH is higher than 12 the S^{2-} dominates. Gutierrez evaluated the effects of long-term pH effect using a laboratory scale anaerobic sewer reactor set. Continuous pH increase to 8.6–9.0 considerably reduced SRB activities. So not only less H_2S is produced but due to its presence in the form of HS^{-} it did not pass liquid-gas interphase. The H_2S production rate of the biofilm was reduced by 30%

at pH 8.6 and 50% at pH 9.0, in comparison to without pH control (The pH in the wastewater is around 7.6) .

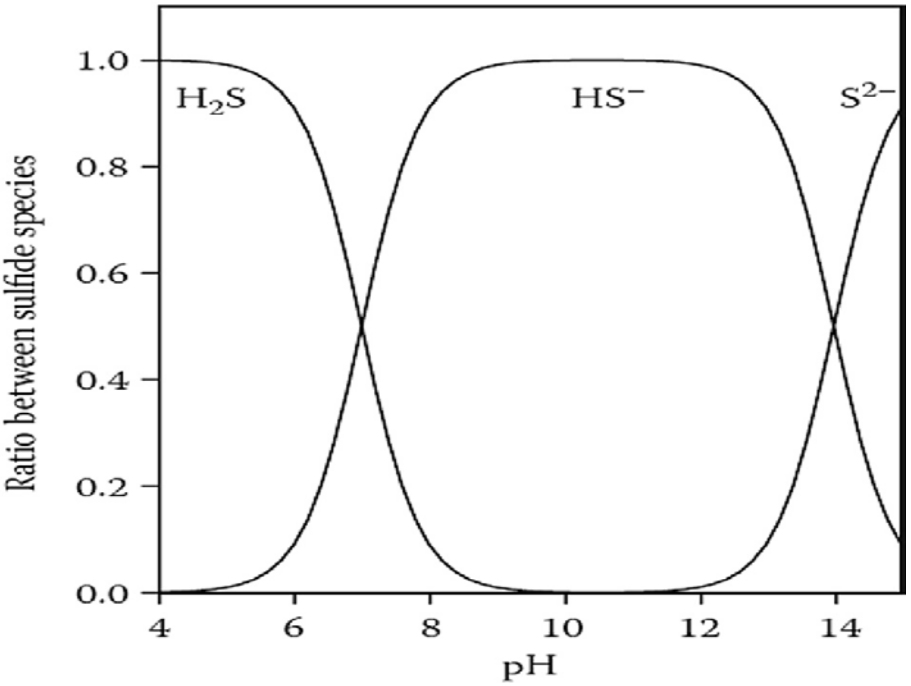

Figure 2.1: Effect of pH on hydrogen sulfide species distribution (Churchill & Elmer 1999).

Equilibrium considerations result in the following equations:

$K_{a,1}= [H^+]*[HS^-]/[H_2S]$ [3]

$K_{a,2} = [H^+] [S^{2-}] / [HS^-]$ [4]

$\mathrm{Log}\frac{[\mathrm{H}S^-]}{[\mathrm{H_2}S(\mathrm{aq})]} = \mathrm{pH} - \mathrm{pK}_{a,1}$ [5]

$\mathrm{Log}\frac{[S^{2-}]}{[\mathrm{HS^-(aq)}]} = \mathrm{pH} - \mathrm{pK}_{a,2}$ [6]

$K_{a,1} = 9.1 \times 10^{-8}$ [7]

$\mathrm{K}_{a,2} = 1.3 \times 10^{-13}$ [8]

$\mathrm{pH} - 7.04 = \mathrm{Log}\frac{[\mathrm{H}S^-]}{[\mathrm{H_2S(aq)}]}$ [9]

$$\mathrm{pH} - 12.89 = \mathrm{Log}\frac{[S^{2-}]}{[\mathrm{HS}^{-}(\mathrm{aq})]} \qquad [10]$$

Where $pK_{a,1}$ = negative logarithm of the H_2S/HS^- equilibrium constant (≈7.04) and $pK_{a,2}$ is the negative logarithm of S^{2-}/HS^- equilibrium (~12.89). The pKa values are for typical wastewater conditions.

Equations 2-6 indicate that acid environments change the H_2S distribution in the direction of increasing H_2S (aq) species fraction, involving higher emission rates, while alkaline (high pH) conditions reduce the H_2S (aq) fraction. Equilibrium between concentration of H_2S in liquid and gas phase is controlled be Henry's law:

$$H^{cc}=c_a/c_g \qquad [11]$$

Where, H^{cc} is the dimensionless Henry's constant. C_a and C_g are concentrations in aqueous and gas phases [mg/L]

$$H^{cp}=C_a/P \qquad [12]$$

where H^{cp} (mole L^{-1} atm^{-1}) is Henry's solubility constant defined via concentration and P is the partial pressure of that species in the gas phase under equilibrium conditions.

2.1.4 Temperature

Temperature is another significant factor, which affects the activity of SRB; a maximum H_2S production rate was detected at 35 °C(Moosa, S, Nemati, M & Harrison, STL 2005). A less amount of oxygen dissolves into the sewer at a higher temperature, but microbial activity would be higher. As a result of microbial activity, oxygen consumption increases with the temperature of the wastewater. (Nielsen, PH, Raunkjær & Hvitved-

Jacobsen 1998). It will help to create an anaerobic environment of the sewer which enables utilization of sulfate as an alternative source of oxygen producing hydrogen sulfide.

At low temperatures (around 9° C), the gravity sewer turns to aerobic condition (1–2 g O_2 m^{-3}). It helps to decrease the dissolved sulfide concentration in the wastewater. However, a few degrees increase in temperature changed this condition (14°C periods with DO < 0.1 g m^{-3}). The temperature increase from 9 to 14°C and the electron acceptor conditions changed from being aerobic to being alternating aerobic-anaerobic .

2.1.5 Sewer Hydraulics

High flow velocity affects the sewer corrosion in two different ways. The high-flow-velocity reduces the thickness of the biofilm which in turn reduces the production of sulfide in the sewer. However, a high velocity and velocity gradient increase the turbulence of the wastewater, and it increases the H_2S emission rate which leads to increased sewer corrosion (Thistlethwayte 1972). The area to volume ratio also increases the production of hydrogen sulfide per unit of liquid volume, increasing the sulfide concentration, because it makes more surface available for a given volume of water to grow SRB biofilm (Hvitved-Jacobsen, Vollertsen & Nielsen 2013). Further, the low shear stress in gravity sewers will indicate a less aeration rate, which creates the anaerobic condition. This will ultimately increase the production of dissolved sulfide (Park et al. 2014a). Table 1.2 shows the Summary of the Chemical, biological and hydraulic conditions that prevail in sewers.

Table 2.1 Summary of the Chemical, biological and hydraulic conditions that prevail in sewers related to the sewer corrosion.

Considered	Conditions that prevail in sewers

Parameter	
Sulfide (S^{2-})	- Minor problems of corrosion: 0.1–0.5 mg S L^{-1}. - Severe concrete corrosion : 2.0 mg S L^{-1} (Gudjonsson, Vollertsen & Hvitved-Jacobsen 2002)
Sulfate (SO_4^{2-})	- In domestic wastewater: 40–200 mgL^{-1}. - Aluminum sulfate addition in water treatment as coagulant contributes substantially to the sulfate level in the sewer (Araújo et al. 2000)
pH	- The lowest pH levels (7.2–7.5) early morning hours and the hours before midnight. - Peak levels of 8.5–8.7 around 8:00 to 9:00 am and second pH peak around 4:00 to 5:00 pm. In Queensland, Australia. Geelong, Victoria, Australia (Sharma, Ganigue & Yuan 2013)
Temperature	- Maximum H_2S production: 35 °C (Moosa, S, Nemati, M & Harrison, STL 2005)
Sewer Hydraulics	- Self-cleansing velocity of 0.6 m/s Low flow velocity, V ($V < 0.8$ m/s), medium flow velocity (0.8 m/s $\leq V \leq 1.5$ m/s) and high flow velocity ($V > 1.5$ m/s) (Santry 1963) - The area to volume ratio varies from place to place. - The shear stress is related to pipe slope as well as depth of flow and consequently (Park et al. 2014b)
BOM	- The industrial wastewater BOM concentration is higher than the

	residential wastewater (Hvitved-Jacobsen, Vollertsen & Nielsen 2013).

2.2 Chemical mitigation strategies of hydrogen sulfide

To mitigate the corrosion, some techniques have been considered. The leading methods developed to date to moderate effects of H_2S have been the dosage of chemicals to the wastewater. For each method, there is a wide range of cost reported , suggesting that there is a lack of understanding of control process.

Australian water utilities use five chemicals to control the H_2S . They are:

- Metal salts
- oxygen
- magnesium hydroxide
- nitrate
- sodium hydroxide

Most of the time, dissolved sulfide is removed from the sewer by precipitation and oxidation. If both oxidation and precipitation happen in the sewer, there will be less chance for the dissolved sulfide to be released to the atmospheric portion of the sewer. Further, activities of the SRB can be minimized by creating a toxic environment for them.

2.2.1 Addition of Metal salts

The dissolved sulfide in the wastewater will react with the metal and form insoluble metallic sulfide (Nielsen, Asbjørn Haaning et al. 2005). Precipitation of metal sulfides removes dissolved sulfide from the liquid phase. As a result, accessible sulfide for release to the sewer atmosphere is reduced. Ferrous, copper, zinc, nickel, and manganese are some of the insoluble metal sulfides that can be formed in the wastewater to reduce soluble sulfide (Nielsen, Asbjørn Haaning et al. 2005).

Iron salts

Iron is the most abundant metal in urban sewer lines. The addition of iron salts such as ferrous chloride, ferric chloride is the most commonly used method for controlling the dissolved sulfide concentration (Nielsen, Asbjørn Haaning et al. 2005; Zhang, Lishan, Keller & Yuan 2009). Iron does not prevent the formation of H_2S but binds the produced sulfide-preventing its transfer into the gas phase. There are some contradictions reported about the effectiveness of the iron salt. According to Jameel (Jameel 1989), ferrous chloride is more than two times effective in controlling the dissolved sulfide concentration than ferric chloride. However, Tomar and Abdullah (Tomar & Abdullah 1994) reported ferric chloride to be more effective than ferrous chloride, indicating the lack of understanding and possibly ignorance of some additional parameters.

Ferric iron (Fe^{3+}) oxidizes sulfide to elemental sulfur (S^o) and the oxidizing reaction forms Fe^{2+} which removes dissolved sulfide by forming FeS, but the reaction of Fe^{3+} is considerably slower than Fe^{2+} (Hvitved-Jacobsen, Vollertsen & Nielsen 2013).

$$2Fe^{3+}{}_{(aq)} + HS^{-}{}_{(aq)} \rightarrow 2Fe^{2+}{}_{(aq)} + S^{0}{}_{(s)} + H^{+}{}_{(aq)} \qquad [13]$$

A combination of ferrous and ferric salts is more effective for sulfide removal in comparison with either salt alone (Padival, Kimbell & Redner 1995). They reported that the reduction in the gaseous phase is not according to equilibrium (Equations 2-6) and precipitation (Equation 7-8) when the reaction occurred at different pH. The concentration level of iron, which is typically 0.4–1.5 mgL^{-1}, suggests the formation of iron sulfide to be an important process of the sulfur cycle in wastewater, because of its importance in governing the dissolved sulfide concentration (Henze 1997); (Nielsen, Asbjørn Haaning et al. 2005).

The reactions of dissolved iron and sulfide species in municipal sewer have so far not been completely quantified. When ferrous (Fe^{2+}) and ferric (Fe^{3+}) salts are used to decrease sulfide in sewage to 0.1 mgS/L the following minimal molar ratios needed. .

Fe^{2+}: S^{2-}	1.3:1
Fe^{3+}: S^{2-}	0.9 :1

The combination of Fe^{3+} and Fe^{2+} in the ratio of 2 to 1 can be used (Firer, Friedler & Lahav 2008).

When Ferrous is used to capture sulfide in the wastewater, ferrous sulfide (FeS) is the main precipitation component. Other compounds such as FeS_2, Fe_2S_3, Fe_3S_4 are rarely formed at equilibrium, and sometimes they do not exist at all (Firer, Friedler & Lahav 2008). The pH and alkalinity have been found as generally affecting parameters for FeS formation. Temperature contributes to a negligible effect by changing ionic strength at low pH <7.5 for the reaction of iron and sulfide (Firer, Friedler & Lahav 2008).

In the low Fe(II) to S(-II) molar ratios (0.5:1 to 0.7:1), the sulfide removal in the laboratory was slightly better than expected. Firer (Firer, Friedler & Lahav 2008) has given following four reasons explaining the phenomena. In actual sewage, sulfide undergoes more reactions: (1) React with other heavy metals, same as FeS precipitation; (2) Oxidation of sulfide; (3) Escape to the air and (4) Measurement errors.

Further, they claim that even when molar ratio was more than 0.9 to 1, results showed a little lower sulfide removal. They propose Fe^{2+} may react with something else such as CO_3^{2-}

(Firer, Friedler & Lahav 2008). In summary, more sulfide removal than the theoretically predicted amount was observed in real sewer and some explanation has been given.

2.2.2 Addition of oxygen

The chemical, as well as biological oxidation, can occur if there is electron acceptor such as oxygen or nitrate present in the sewer (Transfer & Pomeroy 1974). Oxygen addition is a good option where SRB activity is the highest as it is comparatively cheap and effective. The solubility of oxygen in water is dependent on the concentration of oxygen in the gaseous phase (21% for the air). When a pure oxygen is used in pressurized mains oxygen concentration of 45–50 mgL^{-1} can be achieved .

The supply of air (or oxygen) prevents the anaerobic environments, and oxygen can oxidize the dissolved sulfide to sulfate SO_4^{2-} and elemental sulfur (S_0) (Zhang, Lehua et al. 2008);(Nielsen, Asbjørn H, Vollertsen & Hvitved-Jacobsen 2003). Oxygen did not effect the sulfide production ability of the biofilm, but it is effective in delaying the sulfide accumulation in the sewer by oxidizing into thiosulfate and sulfate (Gutierrez et al. 2008).

$$2HS^- + 4O_2 \rightarrow 2SO_4^{2-} + 2H^+ \quad [14]$$

$$2HS^- + O_2 \rightarrow 2S_0 + 2OH^- \quad [15]$$

$$2HS^- + 2O_2 \rightarrow S_2O_3^{2-} + H_2O \quad [16]$$

Chen et al. found that there is a relationship among the initial oxidation rate and the length of the induction period. Further, they reported that polysulfides, such as S_4^{2-} and S_5^{2-} are formed from a reaction between S^0 and S^{2-}. They claim that there is a possibility to oxygenate sulfide in the interface of oxygen and sulfide layers to undergo a sulfide-sulfur-polysulfide cycle, with the initial oxidation of sulfide to sulfur as a rate-determining step

(Chen & Morris 1972). Pourbaix diagram (Figure 2.2) also gives evidences that if we can increase the electro chemical potential in the wastewater by adding oxidising agent such as Oxygen, $H_2S_{(aq)}$ will not exist in the system. It is oxidised to SO_4^{2-}.

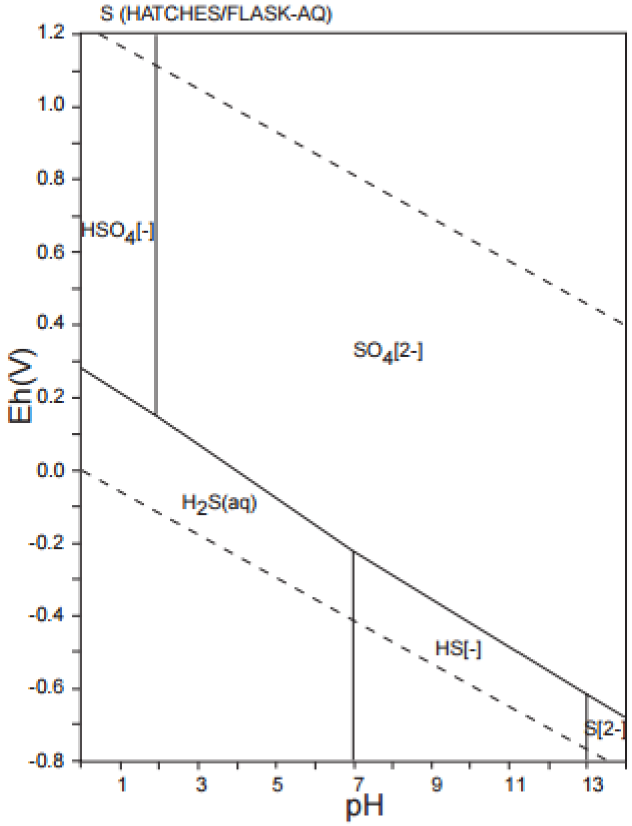

Figure 2.2: Eh-pH diagrams of the system S-O-H(Takeno 2005)

Since sulfide accumulation in the sewer can be minimized by maintaining sewer in aerobic conditions, oxygen accepts the electrons and organic matters will be converted to carbon dioxide (CO_2). Hence, oxygen injection increases carbon consumption in the wastewater, but it did not affect the ability of the biofilm to convert sulfate, even after 120 days of oxygen contact(Gutierrez et al. 2008). This can probably be explained by a rapid consumption of oxygen by aerobic bacteria in the bulk liquid and surface biofilm where H_2S is produced is not being affected.

Understandably, the problem (H_2S production increases) worsens when the temperature increases. The increased temperature stimulates metabolism of aerobic bacteria and depletes the DO levels. When the temperature is increased, the sewer turns anaerobic for a part of the day(Gudjonsson, Vollertsen & Hvitved-Jacobsen 2002). On the other hand, Gudjonsson (2002) has reported that at low temperatures, the gravity sewer was strictly aerobic (DO>2mg/L).

According to Mohanakrishnan in 2008 an injection of oxygen 15-25 mg O_2 per pump event reduced total sulfide discharge levels by 65%. Oxygen is an effective chemical as well as biological sulfide oxidant but does not stop sulfide production. These results suggest that optimization of oxygen addition is essential for maximum efficiency (mg H_2S oxidize/ mg O_2) in controlling dissolved sulfide concentrations in sewers(Mohanakrishnan 2008).

Unfortunately, oxygen injection leads to removal of BOM by consuming valuable and often limited volatile fatty acids which are needed for wastewater treatment downstream (Hvitved-Jacobsen, Raunkjær & Nielsen 1995). This is another argument apart from the excessive cost of oxygen dosing to aim to make oxygen reaction more selective in oxidizing H_2S and limiting the reaction with BOM.

2.2.3 Metal hydroxides

The addition of metal hydroxides such as magnesium hydroxide, $Mg(OH)_2$, and sodium hydroxide (NaOH) to raise the pH of the sewer, is used to reduce H_2S emission to the gaseous phase (headspace) of the sewer systems. (Hvitved-Jacobsen, Vollertsen & Nielsen 2013). $Mg(OH)_2$ increases the pH of sewer up to a maximum value of 9.0, but the increase was gradual because of its limited water solubility . However, NaOH addition applied as a periodic “shock dosing” of wastewater to achieve a pH of 12.5 - 13 for a short period interferes with biofilm and its production of H_2S. The impact of this treatment is limited to a short time (days) and needs to be repeated.

2.2.4 Addition of nitrate

The addition of nitrate has been another chemical dosing method applied for the control of sulfide in sewer systems(Boon 1995; Zhang, Lehua et al. 2008). Injection of nitrate (NO_3^-) to an anaerobic wastewater will form anoxic environments (De Lomas et al. 2006; Haveman, Greene & Voordouw 2005). Jiang et al. have reported that various nitrate salts such as $NaNO_3$, NH_4NO_3, $Ca(NO_3)_2$ were used for the last 70 years to control hydrogen sulfide in sewers (Jiang et al. 2009). Rodriguez-Gomez et al. have reported that 5 mg-N.L^{-1} of nitrate was capable of controlling sulfide production in a 61 km long gravity sewer system. They have used calcium nitrate ($Ca (NO_3)_2$) as NO_3^- source (Rodríguez-Gómez et al. 2005). The mechanism of nitrate reduction of H_2S production is that it provides a preferential source of oxygen (electron acceptor) to sulfate, and SRB is outcompeted by bacteria using nitrate. However, nitrate is not capable of oxidizing dissolved sulfide to the same extent as oxygen .

2.2.5 Other methods

Strong electron acceptor has also been used for the chemical sulfide oxidation (H_2O_2, NaOCl or $KMnO_4$) , (Tomar & Abdullah 1994). Cadena and Peters reported that in laboratory

Chlorine	4.2g
Hydrogen peroxide	2.4g
Potassium permanganate	11.8g

were required to oxidize 1 g of sulfide (Cadena & Peters 1988). The desirable reaction of H_2S with various oxidant are shown as follows:

$$4HOCl + H_2S \rightarrow SO_4^{-2} + 6H^+ + 4Cl^- \qquad [17]$$

$$H_2S + H_2O_2 \rightarrow 2H_2O + S \qquad [18]$$

$$3H_2S + 8KMnO_4 \rightarrow 2H_2O + 3K_2SO_4 + 2KOH + 8MnO_2 \qquad [19]$$

Unfortunately, oxidants are also consumed to further oxidation of product(s) and oxidation of BOM, which reduces the effectiveness of the control measures and increases the cost.

2.3 Design of experimental setups

2.3.1 Reported laboratory scale experimental setups

Moosa et al., (2002) did a kinetic study on anaerobic reduction of sulfate in 2002 using bioreactors with a capacity of 1 L (Moosa, Nemati & Harrison 2002). Figure 2.3 shows the diagram of the experimental set-up. The temperature of 35^0C, pH of 8±0.2 and an anaerobic condition were maintained throughout the experiment. A mixed culture of anaerobic bacteria (acidogenic bacteria, methanogenic bacteria, and SRB) was used for the growth of anaerobic microorganisms in the reactor. Sodium sulfate was used as a source of sulfate (2.5 kg m^{-3}), and sodium acetate was used as the organic carbon source. Other essential organic substrates, inorganic salts, and trace metals were also used. After sulfate 90% to 95% the reduction was achieved, the bioreactors were switched to continuous mode.

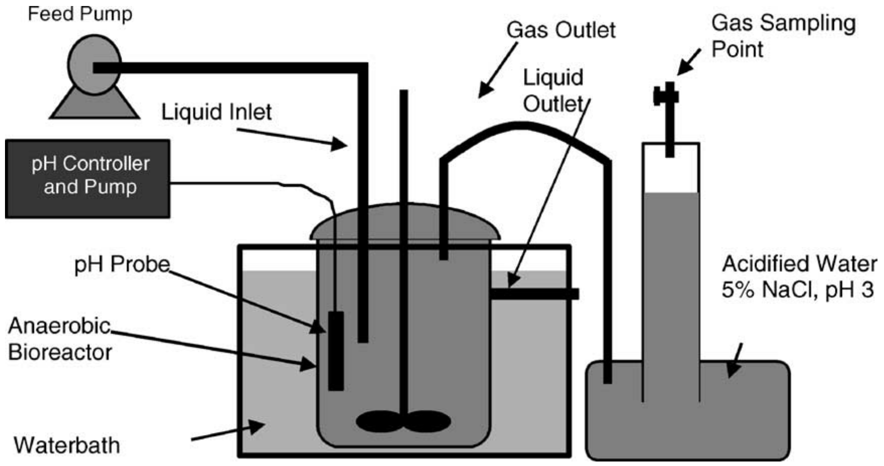

Figure 2.3: Schematic diagram of the experimental set-up (Moosa, Nemati & Harrison 2002)

Moosa at al. used the same bioreactor which he used in 2002 (Figure 2.3) to study the effects of temperature on the kinetics of anaerobic sulfate reduction (Moosa, S, Nemati, M & Harrison, ST 2005).

Yongsiri et al. (2004) studied about the air-water transfer of hydrogen sulfide: an approach for application in sewer networks . Two parallel reactor setups were run, using one to determine the loss of sulfide through emission and the other reactor was used to measure the increases in dissolved oxygen in water because of reaeration. Deionized water was used for the experiments. The volumes of the water and air phases in the vessel were 2.50L and 0.87 L, respectively. The temperature was maintained at 20 ± 0.3^oC. As sulfide sources, $Na_2S.9H_2O$ was used, and the pH was adjusted using the phosphate buffer solution. Initially, dissolved oxygen was removed from the water using nitrogen gas. Dissolved sulfide and oxygen levels were monitored with the time.

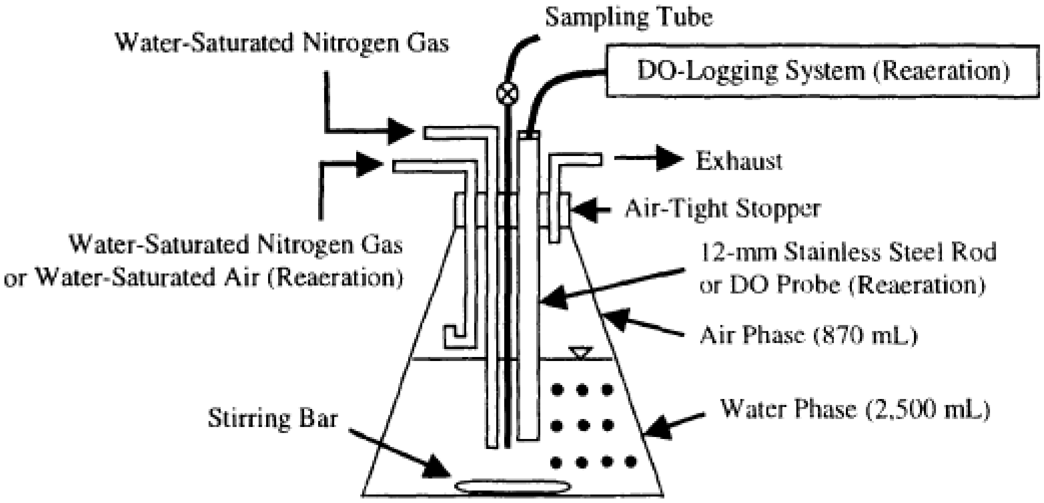

Figure 2.4: Experimental setup for air-water transfer of hydrogen sulfide and reaeration (Yongsiri et al. 2004).

Yongsiri et al. (Yongsiri, Vollertsen & Hvitved-Jacobsen 2004) studied the effect of temperature on the air-Water transfer of H_2S using the same experimental setup as he used to study for air–water transfer of H_2S: an approach for application in sewer networks in 2002 (Yongsiri, Vollertsen & Hvitved-Jacobsen 2002). In 2005, Yongsiri et al. studied the influence of wastewater constituents on H_2S using the same experimental setup as 2004 (Figure 2.4) using both waste water and deionized water(Yongsiri, Vollertsen & Hvitved-Jacobsen 2005).

Nielsen et al. used a reactor set to find out the sulfide–ion interactions in domestic wastewater from a gravity sewer in 2005 (Nielsen, Asbjørn Haaning et al. 2005). For their experimental setup Figure 2.5, they used a 3L water-jacketed reactor. Throughout the experiments, the reactor was filled with wastewater. The temperature was controlled at 15^{o}C. pH, oxidation reduction potential, DO concentrations, Fe(II), Fe(III), total sulfide and metal sulfide were monitored.

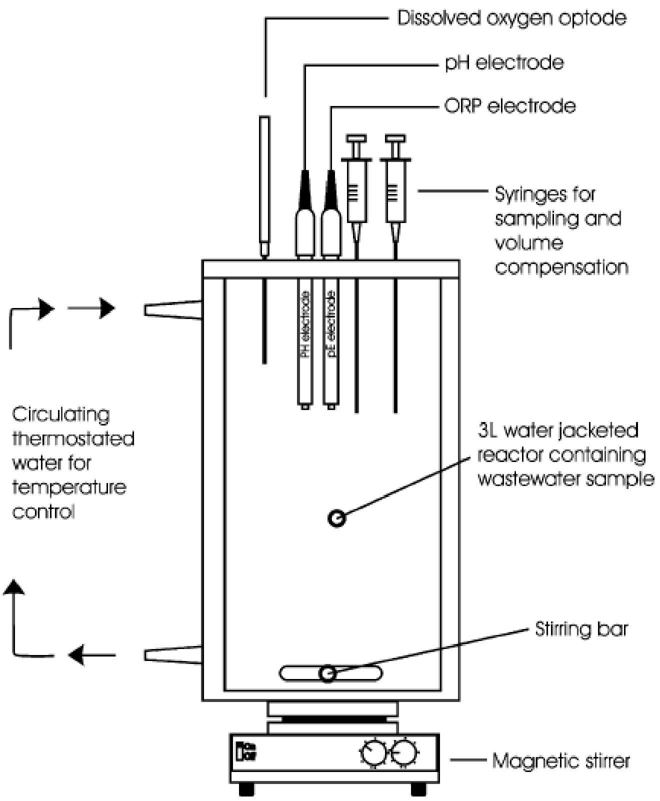

Figure 2.5: Reactor used for studying sulfide – iron interactions in sewer wastewater(Nielsen, Asbjørn Haaning et al. 2005).

Lahav et al. conducted twenty experiments (duration each experiment between 1 to 4 hours) for predicting $H_2S(g)$ emission rates in gravity sewers using 27m long PVC sewer pipe, with an internal diameter of 0.16 m (Figure 2.6). Na_2S dissolved in tap water (pH around 7.8, alkalinity 180–200 mg/L as $CaCO_3$, DO of about 6 mg/L and sulfate of about 20mg S/L) was used as sulfide source. After each experiment, the system was dried to ensure no biofilm is formed. Chemical sulfide oxidation was not considered .

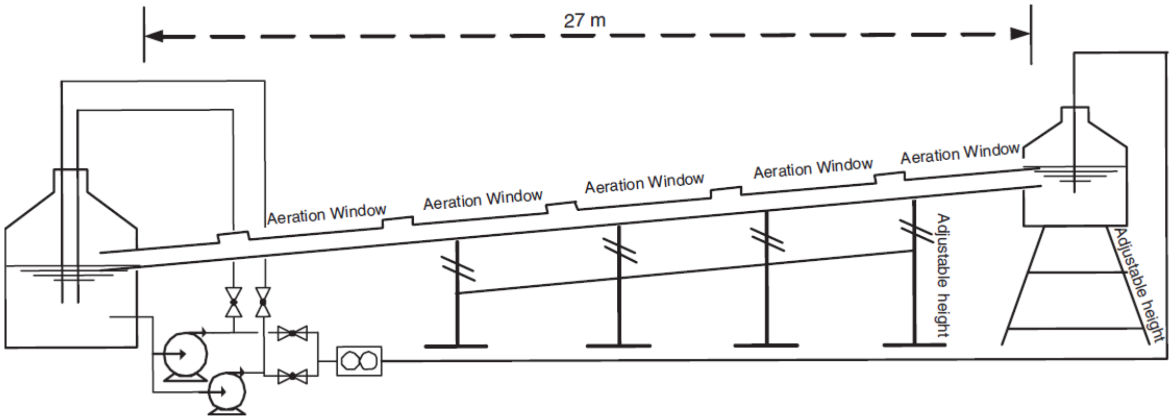

Figure 2.6: Schematic layout of the PVC experimental sewer and auxiliary systems (Lahav, Sagiv & Friedler 2006)

Jegatheesan et al. in their research , used an 18 m long PVC sewer pipe with an internal diameter of 0.15 m for estimating H_2S dissipation rate constant under the influence of different chemical dosing (Figure 2.7). Six percent of the total pipe length was exposed to the atmosphere. Na_2S was used as sulfide source. They studied the dissipation of sulfide with the addition of $Mg(OH)_2$, NaOH, $FeCl_3$ and $Ca(NO_3)_2$ and the dissipation rate is estimated as a function of hydraulic parameters such as the slope and the velocity gradient of the sewer. Their group presented models in 2016 for H_2S gas emission and the performance of ideal dosage of suppressing chemicals using the same laboratory scale sewer system, they have used in 2015(Abdikheibari et al. 2016). In this experimental setup, they have measured the H_2S concentration in the gas phase using OdaLog instrument.

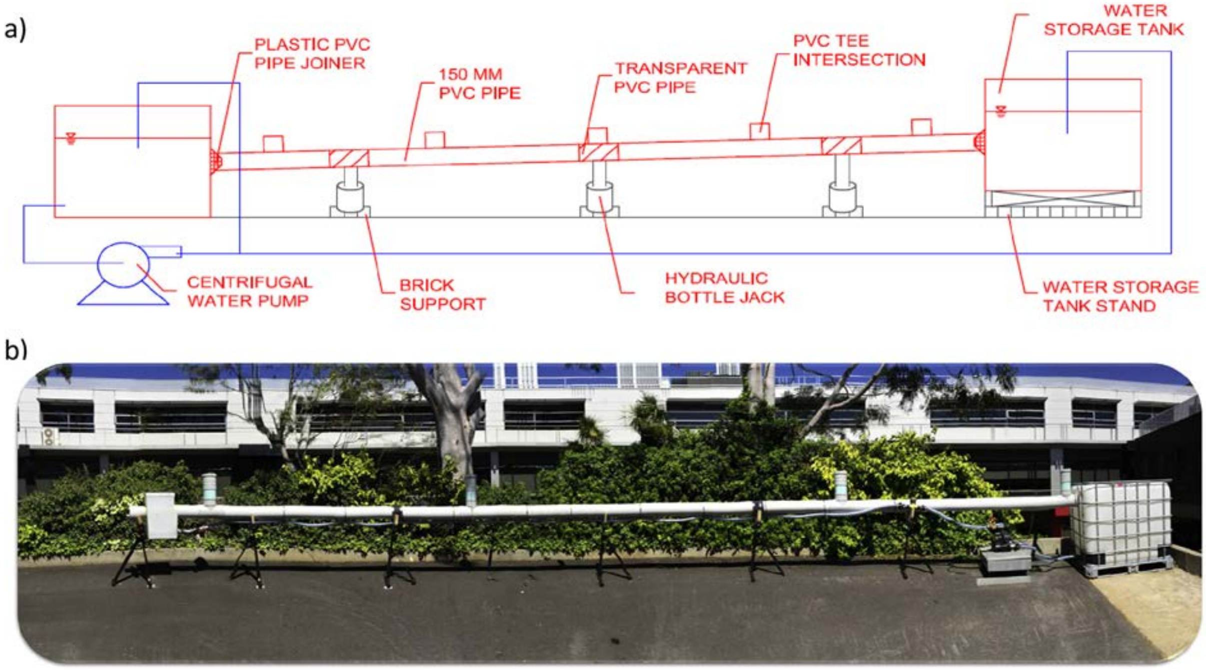

Figure 2.7: Experimental sewer (a) schematic (b) actual experimental rig (Jegatheesan et al. 2015)

2.3.2 Comparison summary of the laboratory scale sewer systems with real sewer system

Table 2.2: Comparison summary of the laboratory scale sewer systems from previous research

Literatures	Similarities with real sewer system	Shortcomings
(Yongsiri, Vollertsen & Hvitved-Jacobsen 2004)	The hydraulic condition was created using a magnetic stirrer. The pH was controlled. An oxygen concentration was monitored.	Na_2S dissolved in deionized water was used as a medium. In real sewer, H_2S is continuously produced. Gas phase concentrations were not measured
(Nielsen, Asbjørn Haaning et al. 2005)	Hydraulic conditions were created using a magnetic stirrer. The temperature was controlled. Raw wastewater was used	There is no gas phase in the system.
(Lahav, Sagiv & Friedler 2006)	Created a flow in the system, 27 m long PVC sewer pipe was used.	Chemical sulfide oxidation was not considered. Na_2S dissolved in tap water was used as a medium
(Jegatheesan et al. 2015)	18 m long PVC sewer pipe was used. Effect of hydraulics was considered.	Na_2S was used as a sulfide source. Chemical sulfide oxidation was considered. Gas phase samples were not taken but was calculated according to the liquid phase H_2S concentration.
(Abdikheibari et al. 2016)	18 m long PVC sewer pipe was used. Effect of hydraulics was considered. Gas phase H_2S concentration was measured.	Na_2S was used as a sulfide source.

(Sharma et al. 2014)	Sewer biofilm was grown. Created a flow in the system. Real wastewater was used	Gas phase measurements were not taken

In conclusion, most of the designed experimental setups in past did not represent the actual sewer system. Therefore, a new design for experimental setup was needed.

Chapter 3 : Rector design

3.1 Design considerations

A significant number of studies have been carried out around the world using various kinds of laboratory scale reactor sets to identify the effectiveness of chemical dosing methods to control the H_2S formation in sewer thus to mitigate sewer corrosion. However, following combination of factors have not been considered together while designing the reactors:

- Gas phase sampling ports and measurement methods
- Growing a biofilm to produce H_2S simulating a real sewer rather than using chemicals
- Considering actual velocity of the gravity sewer
- Simulating air leaks and thus oxygen presence in headspace of real sewer systems
- Effect of the temperature

3.2 Reactor set up and operation

Two high-density polyethylene (HDPE) Buckets (11 L) were used as the reactors. As shown in Figure 3.1, air and liquid sampling ports were placed at the top and near the bottom of the bucket. Both reactors were closed using airtight plastic lids. A concrete layer was placed at the bottom of each reactor to grow biofilms and to simulate the material present in a real sewer system. The outlet tube (length 1 m and diameter 4 mm) connected just above the water level was kept open to the atmosphere (Figure 3.1) to allow for the partial aeration in the reactor. The black color poly drip irrigation tubes, which block the light, were used in the inlet and outlet to prevent the algal growth. Synthetic wastewater was used as a feed solution and SRB seed (100 mL) collected from an actual sewer was added at the beginning. Feed water rate was maintained at 1L/day. Because of the difficulties in the laboratory environment, maintained feeding water flow rate was less than actual flow rate of the real sewer; however required chemicals and nutrients for the SRB have been simulated. Both reactors were operated in parallel. One reactor was used to dose chemicals whereas the other was used as a control. Observations of the controlling reactor were used to identify the effect of the chemical dosing methods by comparing observation of the other changed reactor. The reactors were manually agitated about half an hour before each sampling. The concentration of H_2S in the liquid and the gas phases of the reactors were monitored on a daily basis.

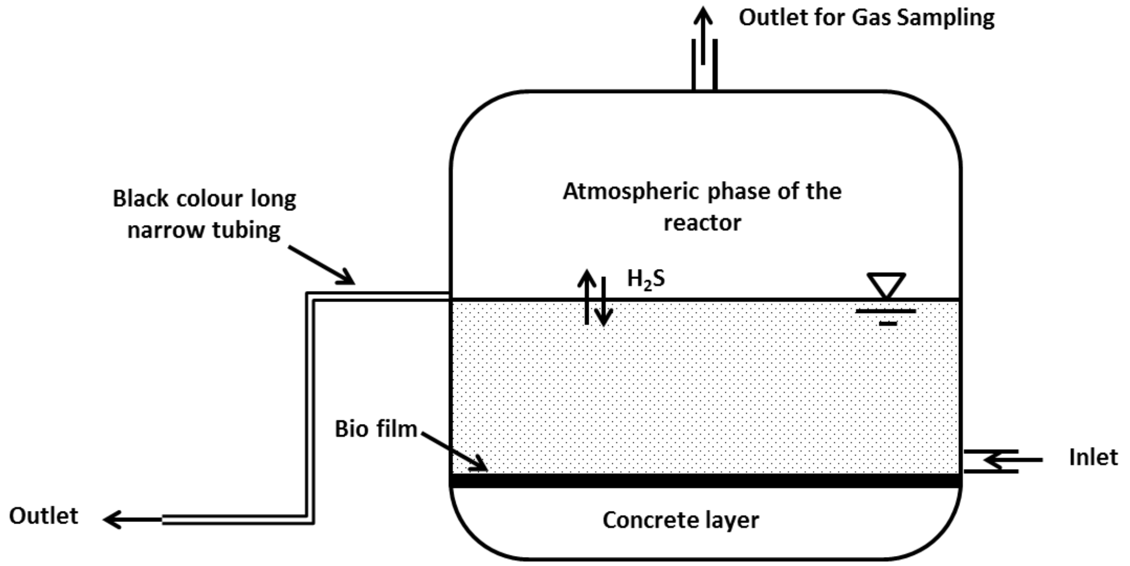

Figure 3.1: Typical setup of the laboratory scale reactor

3.3 Synthetic wastewater composition

Compositions of the synthetic wastewater are shown in Table 3.1. This composition was adopted after several variations and observation of H_2S production. Initially, tap water was used to prepare the feed water but from the day 20 of operation river water was used because tap water helps to accumulate iron inside the reactors. Yeast extract was added from the day 15. Initially sodium acetate was used, but from day 40 ammonium acetate was added to increase the ammonium concentration. The influent DOC concertation of 400 mg/L (~1066 mg COD/L) using the acetate was maintained mainly to increase the production rate of H_2S. The pH was maintained around 7.5 which represents a typical pH in a sewer system.

Table 3.1: Composition of syntheticwastewater

Chemicals	Concentrations (g/L)	Trace metals	Concentrations (g/L)
Ammonium acetate	1	$CoCl_2$:$6H_2O$	0.0015
K_2HPO_4	0.004	$FeCl_2$:$4H_2O$	0.0080
$NaHCO_3$	0.125	$MnCl_2$:$4H_2O$	0.0040
Na_2SO_4	0.37	$NaMoO_4$:$2H_2O$	0.0040
Yeast extract	0.40	$NiCl_2$:$6H_2O$	0.0050

3.4 Comparison of designed reactor set with the actual sewer system

Table 3.2: Comparison between designed laboratory scale sewer system and the actual sewer system

Consideration	**Actual Sewer system**	**Laboratory Scale sewer system**
Growing a biofilm with SRB	Biofilm grows on top of the concrete wall of the liquid phase	Biofilm was grown on the concrete wall of the liquid phase
Importance of H_2S gas phase measurement	In sewer system, corrosion mainly happens on the wall of the gaseous phase	The gas-liquid interface was simulated. Gas sampling facility was developed.
Air explore	Air can enter into the sewer	Air can enter into the

	system mainly through the manholes, but generally, sewer is anaerobic	simulated system through the inflow, outflow and gas phase sampling port but generally, it is anaerobic.
Effect of the temperature	Temperature varies diurnally and seasonally. Mainly underground sewer temperature is lower than the room temperature.	Temperature varies diurnally and seasonally. Higher than the actual sewer (room temperature)
Velocity of the flow	0.55 m/s (self-cleaning gravity flow)	Flow rate: 1L/day,
Wastewater characteristic	Domestic and industrial actual wastewater	Synthetic wastewater with the chemical composition of general wastewater

Comparison of real sewer system with laboratory scale sewer system (Table 3.2) clearly shows that the designed laboratory scale sewer system acceptably simulate the real sewer system. The low flow rate and feeding with the synthetic wastewater can be taken as drawbacks. In actual sewer system, wastewater flows higher than 0.55 m/s. Table 3.3 shows the comparison of hydraulics in experimental reactors and actual sewer system.

Table 3.3: Comparison of hydraulics in experimental reactors and actual sewer system

Sewer hydraulics	Actual sewer system	Laboratory scale sewer system
Area to volume ratio	Depend on the size of the sewer line	It has been simulated acceptably adjusting the depth of the reactor
Flow velocity	Low flow velocity, V (V < 0.8 m/s), medium flow	Flow created only when feeding the reactor, but mixing

	velocity (0.8 m/s ≤ V ≤ 1.5 m/s) and High flow velocity (V > 1.5 m/s) (Santry 1963)	during sampling might have helped to a certain extent.
Shear stress	The shear stress is related to pipe slope as well as depth of flow	Only intermittent mixing during sampling might have produced some effect.
Velocity gradient	High velocity, pipe slope and flow are factors that increase the turbulence	Turbulence created by mixing during sampling.

Chapter 4 : Development of the sulfide mitigation method

For the first 40 days, synthetic wastewater was pumped to the first reactor. After identifying the composition of the synthetic wastewater which can increase activities of SRB, feeding was started for the second reactor. For the first five days, hydrochloric acid (HCl) was used to reduce pH to compensate for concrete leaching and then in the next five days carbon dioxide (CO_2) was bubbled to reduce pH. However, after the first ten days vinegar (acetic acid) was used to maintain the pH 7.6.

4.1 Experiments

4.1.1 Continuous System

To test the effectiveness of control methods, a consistent H_2S production was ensured in both reactors by operating at constant pH 7.6. After achieving a consistent H_2S production (approximately 35 mg/L) in both reactors, $Ca(OH)_2$ which is a cheap source of alkaline was used to control pH. In the beginning, pH was adjusted only in Reactor-1 to 8.0 by adding 30-40 mg/L of $Ca(OH)_2$, keeping Reactor-2 as the controlling reactor (pH 7.6) as detailed in Table 4.1. Samples were collected from both the liquid phase and the gas phase for the analysis. At the same time, sulfate and DOC concentrations were monitored.

Table 4.1: Summery of the experiments

Time		0 - 50 days	50 -70 days	70-80 days	>80 days
Continuous Experiments	Reactor 1	Continuous feeding of the synthetic wastewater and adjustment of pH	Feed synthetic wastewater	Adjust pH to 8 (adding $Ca(OH)_2$) and feed synthetic wastewater	Feed synthetic wastewater
	Reactor 2	Batch feeding of Synthetic wastewater and adjustment of pH	Feed synthetic wastewater	Feed synthetic wastewater (used as controller)	Feed synthetic wastewater
Batch tests	MilliQ water with sodium sulfide (Na_2S), buffered stoichiometrically by $CaCO_3$ and 10% of $FeCl_2$. Measured H_2S in both liquid and gas phases				

4.1.2 Batch Experiments

4.1.2.1 Batch experiment to understand the liquid air equilibrium of H_2S with $FeCl_2$

A series of batch tests was carried out using MilliQ water and sodium sulfide (Na_2S) to identify the reason behind the reactors observations. The pure chemical was used for the batch experiments because it was easy to build up a theoretical explanation for the observation of the reactor experiments. The batch test was done by adding ferrous chloride ($FeCl_2$) 10% of the stoichiometry requirement (Equation 12). H_2S concentrations in the gas and liquid phases of the bottle were measured at different pH values.

4.1.2.1 Batch experiment for understanding the changes in the reaction rates of H_2S with O_2 in the presence of Fe^{2+}

Another series of batch test was carried out using MilliQ water and Na_2S to identify the changes in the reaction rates of H_2S and O_2 in the presence of Fe^{2+}. The solution was buffered by 200 mg l^{-1} sodium bicarbonate ($NaHCO_3$). Dissolved oxygen (DO) concentration was monitored with the time and observed the differences in the reaction rates.

4.2 Analysis

All water samples except for the one collected for sulfide measurement were filtered through pre-washed 0.45 μm polycarbonate membrane filter papers. Before filtering the samples for the DOC measurement, pre-washing was carried out by placing the filter paper on the filtration apparatus and by filtering around 100 mL of Milli-Q water through the filter device for minimizing the contamination from the filter paper into the sample. DOC concentration was measured using Shimadzu TOC-L combustion analyzer. The measurement error for TOC machine was 5%.

As sulfide reacts rapidly with oxygen in the air, the samples for sulfide measurements were not filtered.

Sulfate concentrations of the samples were measured by a turbidimetric method depending on the fact that barium sulfate formed (Standard methods for the examination of water and wastewater 2012), using Thermo Scientific Discrete Analyzer which has an experimental error of 5%.

Dissolved sulfide concentration was measured using DR 2800 Spectrophotometer by Methylene Blue Method (the procedure is equivalent to USEPA method 376.2 and Standard Method 4500-S_2– D for wastewater).

H_2S concentration in the gas phase was measured by sampling gas from the headspace of the reactor into a syringe containing an alkaline solution (pH 10-11), and total sulfide in the solution was measured using Methylene Blue Method. The pH was measured using a portable pH meter.

4.3 Results

4.3.1 Acclimatisation of the sulphate reducing bacteria to produce H_2S

The H_2S production gradually increased in both reactors from the start of supplying synthetic wastewater (Figure 4.1). In the beginning, to prove the methodology only Reactor-1 was continuously fed, and different synthetic wastewater compositions were attempted until identifying the ideal composition for the growth of SRB. pH was reduced from 10-12 to 7.6±0.2. Higher pH was caused by leaching from the fresh concrete surface. The adjustment of pH was carried out using different chemicals (HCl, CO_2, CH_3COOH) to provide conditions similar to a real sewer and to promote the adequate production of H_2S.

To better prepare the concrete surface of Reactor-2, the pH adjustment was carried out independently to prevent leaching (CH_3COOH was identified as the suitable chemical for adjusting pH without disturbing the growth of SRB), and synthetic wastewater was placed to ensure the surface is ready for continuous operation. Such activities helped in the quick production of H_2S from Reactor-2 (Figure 4.1).

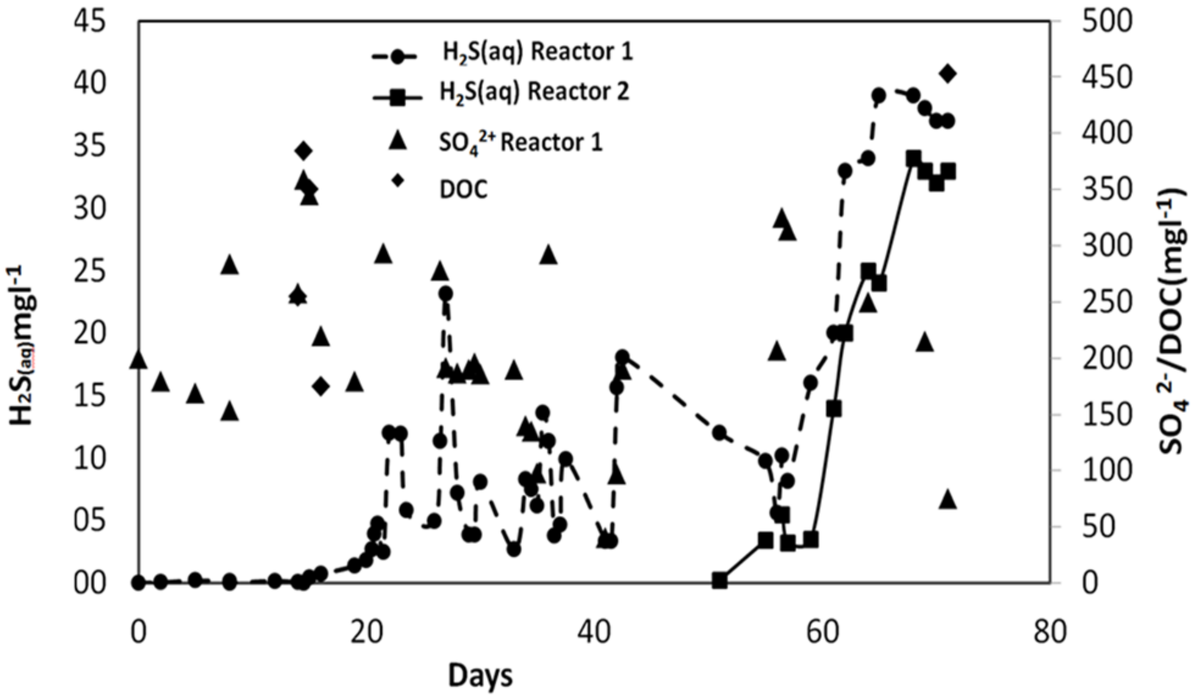

Figure 4.1: H_2S concentration in liquid phase before applying control measure

From Figure 4.1, it can be seen that after 70 days both reactors had similar H_2S concentrations (30-40 mg/L) in the liquid, which may be considered higher value achieved in a real sewer.

4.3.2 Effect of pH to control H_2S production on liquid and gas phases

Increasing pH from 7.6 to8.0 by adding 45 mg of CaO/L in Reactor -1 on 72nd day, sulfide concentration significantly reduced (Figure 4.1). Similarly, further adjustment of pH to 8.4 with a similar amount of CaO on the 77th day, the aqueous sulfide concentration further decreased in Reactor-1. The sulfide concentration includes all the species (H_2S, HS^- and S^{2-}) in the aqueous phase. This phenomenon is similar to what was reported by Sharma (Sharma et al. 2014) when pH was raised. However, the authors observed a significant effect on sulfate reduction when pH was above 8.4. Sharma et al., 2014 explained that such observation was due to inhibition from high pH and free ammonia concentrations. However, in the reactor, total ammonia concentration was maintained constant (220 mg/L) and the changes in free ammonia concentrations, when pH was changed from 7.6 to 8.4, is not sufficient to explain the discrepancy arising from the pH adjustment. Therefore, it could not be used to describe the observed phenomenon. Another possible reason could be the formation of other species such as disulfide that were not measured during the experiment. These species could be formed because of the exposure to atmospheric gasses entering through the long narrow tube on the outlet, or through the gas-sampling vent on the top or when the pressure was reduced from the withdrawal of a liquid sample from the reactor.

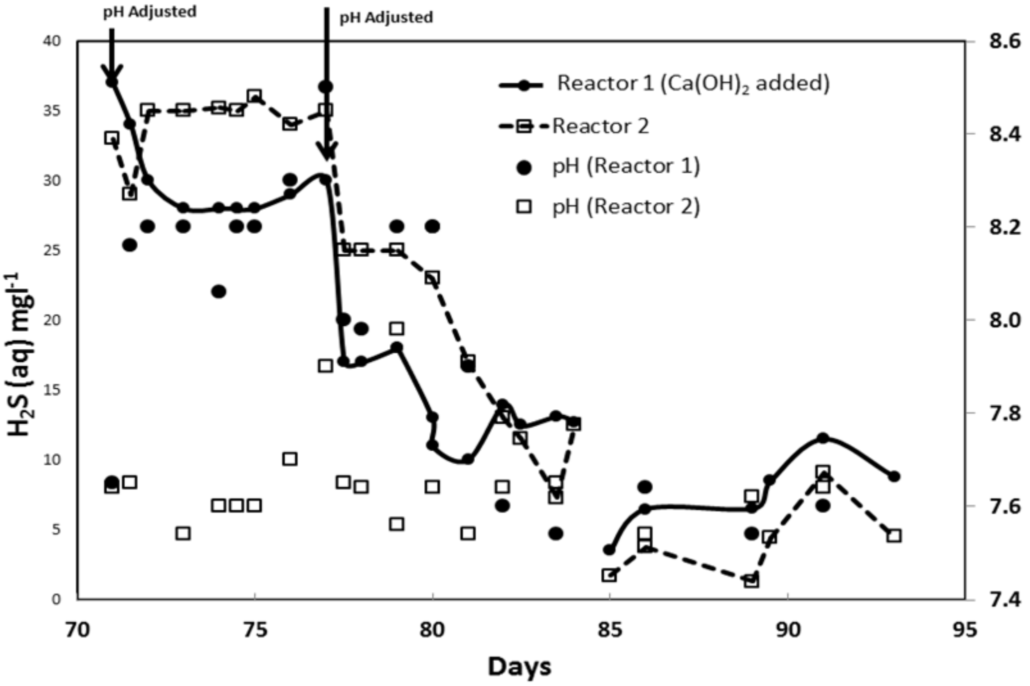

Figure 4.2: H_2S concentrations in liquid phase after controlling pH by adding $Ca(OH)_2$ in Reactor-1

In Figure 4.2, measured gas phase sulfide concentrations were compared with theoretical sulfide values calculated using Eq.10 assuming the sulfide measured in the liquid mainly represent dissolved sulfide ($H_2S+HS^-+S^{2-}$). It is interesting to note that at a lower pH (7.6), gaseous concentrations can be explained by the theoretical calculation, but at higher pH values this cannot be explained (Figure 4.2). The measured sulfide concentration is significantly lower than the theoretical value at higher pH.

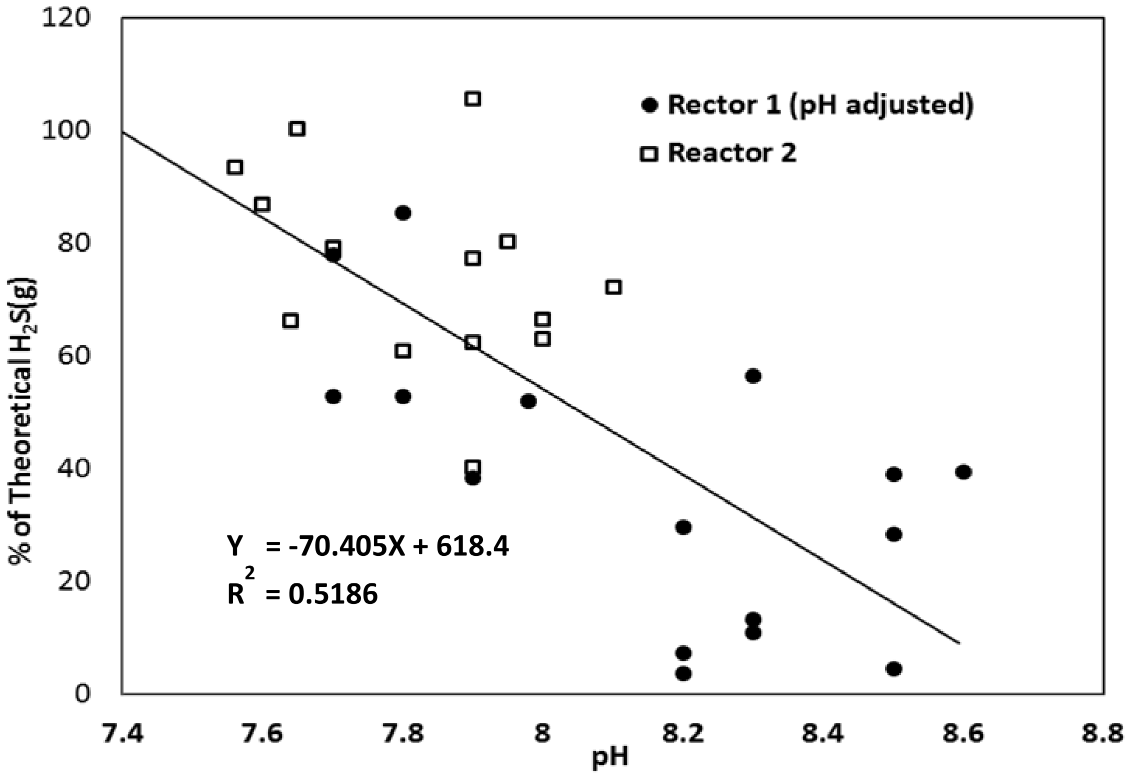

Figure 4.3: Comparison between measured and theoretical $H_2S_{(g)}$ concentrations at different pH

One possible reason could be the formation of metal sulfides that may be accounted during liquid sulfide measurements as it considers a mixture of sulfide species. The reactor was continuously fed and hence there could be a certain amount of metal sulfide within the sample. However, if metal sulfide is present, the saturation close to 100% could not be obtained at pH 7.6 as most of the metals could have been associated with sulfide at this pH.

Therefore, there could be another mechanism for the reduction of sulfide in the gas phase. If the maximum amount of metal sulfide is assumed to be precipitated but still there is a significant discrepancy between the actual gas phase concentration and the theoretical concentration (Figure 4.3).

In summary, the results show that with the slight increase at pH (from 7.6 to 8.2), the gaseous H_2S concentration could be controlled in gravity sewers.

At the same time, the wider fluctuation was identified between measured sulfide concentration with the theoretical value at higher pH. However, to exploit this phenomenon, a series of laboratory experiments including batch experiments were done. Designing of the experiments, observation, result and discussion of the mentioned laboratory experiments are presented in Chapter 5.

Chapter 5 : Experiments to understand the reactor observations

5.1 Batch tests to understand the discrepancy in gaseous H_2S concentrations

Series of batch tests were done to identify the reason for the fluctuation in gaseous phase sulfide concentrations between the measured the theoretical values. In the reactor experiment DO, and a catalytic amount of metal (used as trace metals) could enter into the reactor with the feeding water. According to observations from the batch test (Table 5.1),without $FeCl_2$, the gas phase sulfide measurements matched with theoretical calculation irrespective of whether N_2 gas was bubbled, i.e. the amount of oxygen-limited or not. However, even with an addition of only 10% of the stoichiometric requirement of $FeCl_2$ (Eq. 20), the gas phase concentrations of H_2S substantially reduced.

$$FeCl_2+H_2S \rightarrow FeS+HCl \qquad [20]$$

It would be understandable if the added amount of $FeCl_2$ were equal to the stoichiometric requirement, but in this experiment, only 10% of S^{2-} should be bound with Fe^{2+}. Oxygen availability has also significantly enhanced the reduction of gas phase H_2S, even more than that would be expected based on the theoretical value and liquid phase concentrations (Table 5.1). It is understandable that oxygen in the liquid phase can react with H_2S to form either S^o, $S_2O_3^{2-}$, or SO_4^{2-}. Bubbling of N_2 gas can reduce the amount of oxygen in the water and the headspace, but cannot eliminate it completely. Hence, at pH 8.35 with the bubbling of N_2 gas, a less reduction was noted (Table 5.1).

Influence of the pH on the reaction rate is not easy to explain although the higher pH had revealed a reduction in gas phase concentration when $FeCl_2$ was present in the water, which was not bubbled with the N_2 gas. This observation excludes the microbial contribution as there were no microbes present in test batch samples. It is, however, known that a higher pH value also reduces the production of H_2S by SRB(Al Zuhair, El-Naas & Al Hassani 2008). Therefore, the ingredients for the better control of H_2S in the gas phase of the sewer appear to be the presence of ferrous iron, some oxygen, and a higher pH. The extent to which these parameters are to be maintained needs to be evaluated.

Table 5.1. : Results of the batch experiments

	With N_2 gas bubbling			Without N_2 gas bubbling		
pH	7.65	8.35	8.1	8.1	8.35	7.85
$FeCl_2$ (stoichiometry)	10%	10%	0	0	10%	10%
H_2S(aq) mg/L	14.85	16.00	15.65	15.00	15.14	15.66
H_2S(g) mg/m^3	749	115	369	328	32	164
Theoretical (H_2S)	833	166	372	327	166	556
H_2S(g) % of theoretical H_2S	90	69	99	100	19	29

While the exact mechanism is not known yet, the $FeCl_2$ seems to be catalyzing the reaction with oxygen and forms sulfur compound(s) which could also be measured as H_2S by the method adopted. This implies that the H_2S measurement needs to be improved.

5.2 Effective use of oxygen for H_2S reduction in gas phase

Another set of batch experiments was carried out to understand the reaction between H_2S and oxygen in the reactor water. The atmospheric air which contains 23% (By Weight) oxygen was used as an oxygen source for the experiments. For the first experiment, three pet bottles (200 mL) were filled with reactor water (35 mgL^{-1} H_2S) of 190 mL (10 mL air), 180 mL (20 mL air) and 170 mL (30 mL air) leaving the remaining space for air. Initially DO level of the reactor water was around 1 mg/L. The available O_2 amount in the gas phase of each bottle 2.76 mg, 5.52 mg and 8.27 mg respectively. The H_2S concentration in the liquid was monitored after shaking the bottles at different time intervals. The results of this test are shown in Figure 5.1. According to Figure 5.1, the reaction rate was similar in all three bottles at the beginning. However, in the later stages, H_2S concentration in liquid started to decrease faster in the samples which had higher air volume.

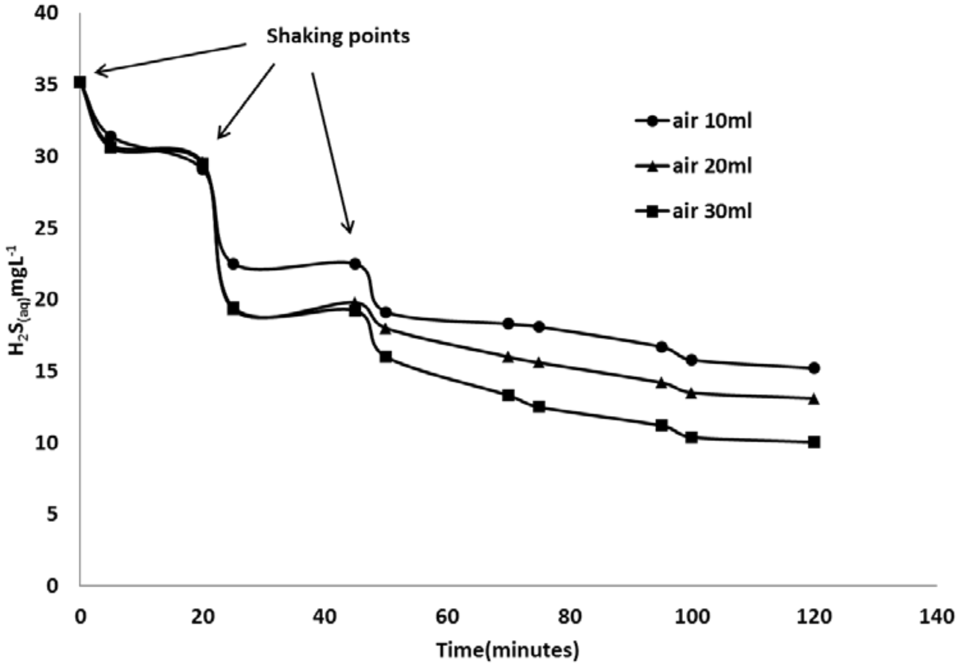

Figure 5.1: H_2S concentration in the reactor water after mixing with different air volumes

In the second experiment, the batch experiment was conducted using the reactor water with the catalytic amount of ferrous iron and observed the reduction of DO concentration with time. The aim of this experiment was to understand the catalytic effect of Fe^{2+} ion in the reaction between H_2S and oxygen. The experiment was conducted using 200 mL pet bottles with 150 mL of reactor water (starting H_2S concertation was 9.3mg/L) with and without a catalytic amount of Fe^{2+} (1mg/L) in two different pH values 7.3 and 8.3. From Figures 5.2 and 5.3, it is clear that in both cases the reaction rate increased in the presence of Fe^{2+}. Further, Figures 5.2, 5.3 show that there is a different oxidation rate at high and low pH. According to the literature (Keller-Lehmann et al. 2006), at low pH, ferric ion acts as a catalyst to oxidize sulfide. From our observation, the catalytical effect is also evident at higher pH (8.3-8.5).

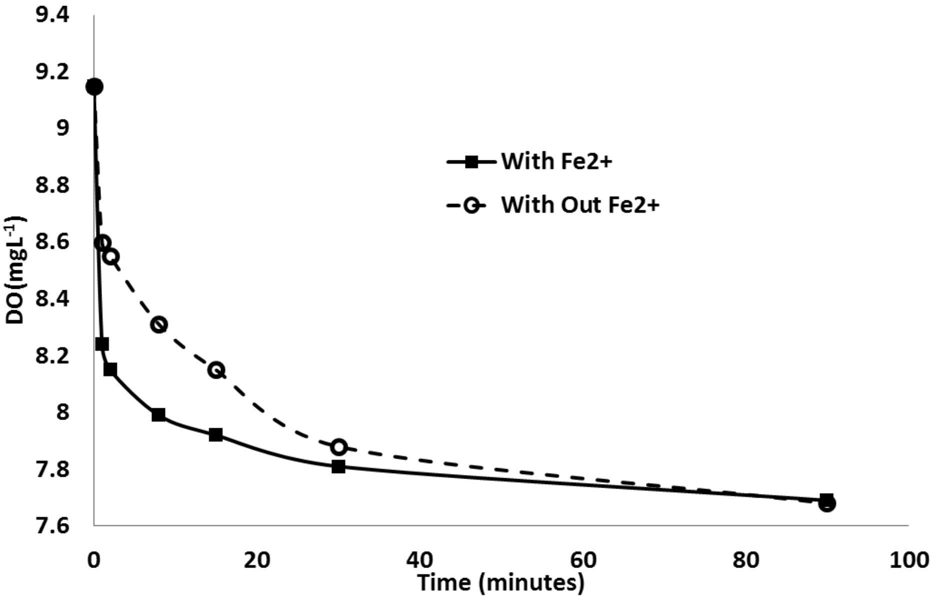

Figure 5.2: DO consumption in reactor water at pH 7.3 with and without Fe^{2+} ion

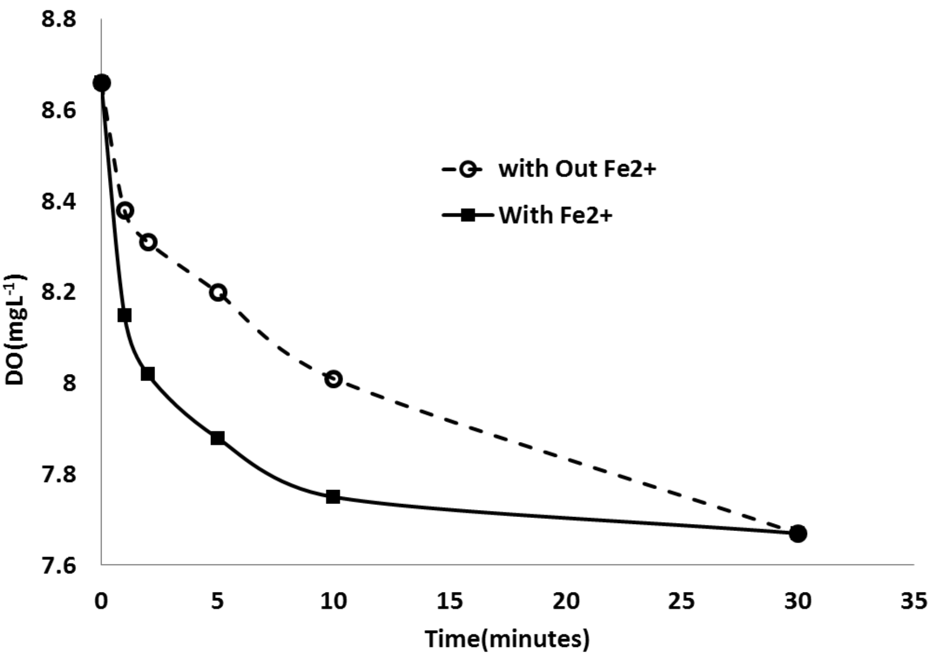

Figure 5.3: DO consumption in reactor water at pH 8.3 with and without Fe^{2+} ion

To further understand the mechanism, third set of experiment was carried out using Na_2S (8.6 mg S/L) containing water and a catalytic amount of Fe^{2+} ion (1mg/L). DO concentration was measured with time. The observation was same as in the previous batch test with the rector water. DO reduction rate was higher in the presence of Fe^{2+} at pH 8.3 (Figure 5.4). The fourth experiment was done using Na_2S (9 mg S/L) containing water and a catalytic amount of Fe^{2+} (1 mg S/L) ion at two different pH (6.8 and 8.7). Similarly, DO reduction rate was high at low pH in the reactor water (Figure 5.5). To exploit the fact that at higher pH microbes produce less H_2S and that lower equilibrium concentrations of H_2S species in the liquid phase prevails, experimental results at higher pH is more interesting to reduce gaseous H_2S concentration.

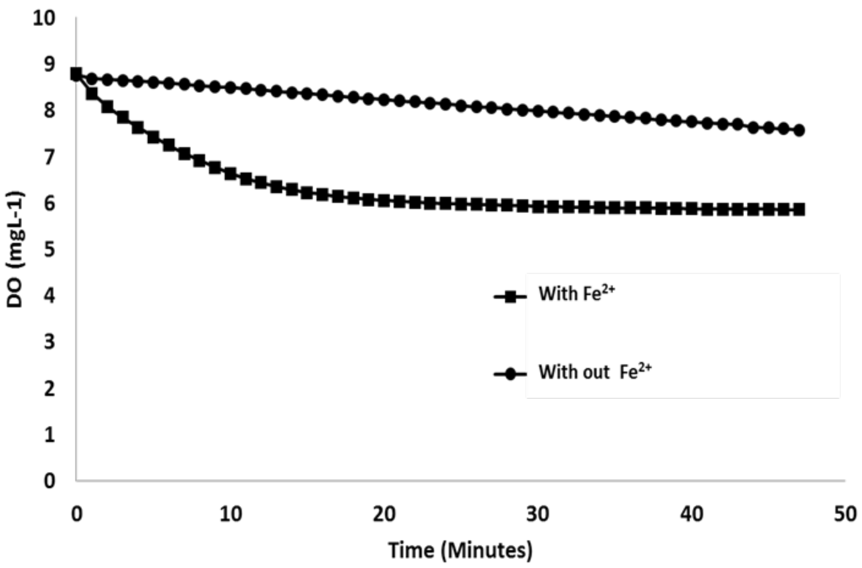

Figure 5.4: DO consumption with Na_2S in aerated MilliQ water buffered by $NaHCO_3$ (200 mg L^{-1}) at pH 8.

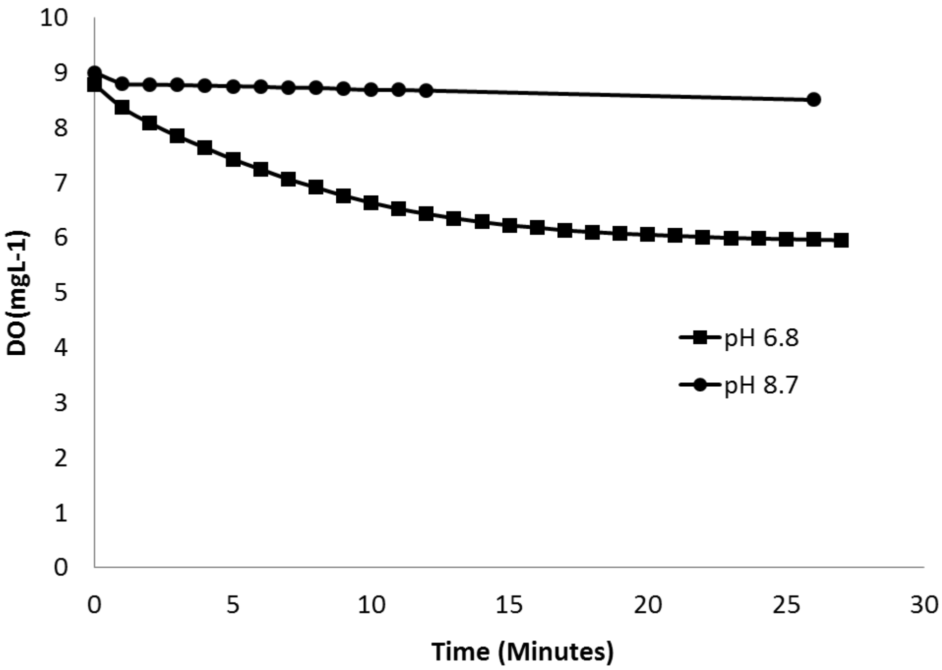

Figure 5.5: DO consumption with Na_2S in aerated MilliQ water buffered by $NaHCO_3$ (200 mg L^{-1}) with Fe^{2+}ion.

5.3 Identifying sulfur compounds in reactor water in the presence of H_2S, Fe^{2+}, and DO at high pH.

5.3.1 Silver nitrate ($AgNO_3$) titration

To understand the behavior of the sulfide oxidation reaction at high pH in the presence of Fe^{2+}, a series of silver nitrate titration tests were carried out using MillQ water and reactor water. A silver electrode with HQ40d meter was used to measure the voltage. Figure 5.6 shows the titration test result obtained from the titration of 4.5 mg of Na_2S with 1g L^{-1} $AgNO_3$ solution. After all S^{2-} ion precipitates in the solution as silver sulfide (AgS), the voltage suddenly increases from -750 mV to near zero (Figure 5.6). The amount of S^{2-} ion in the solution is proportional to the required amount of $AgNO_3$ to achieve the voltage changes. In a similar way, a set of titration tests was conducted using different S^{2-} concentrations and the calibration curve (Figure 5.7) was developed using the titration results. The major advantage of this method is that it can measure S^{2-} in highly turbid water where the colorimetric method is not suitable. The method measures the total sulphide (H_2S+S^{2-}) and depending on the pH the distribution can be determined.

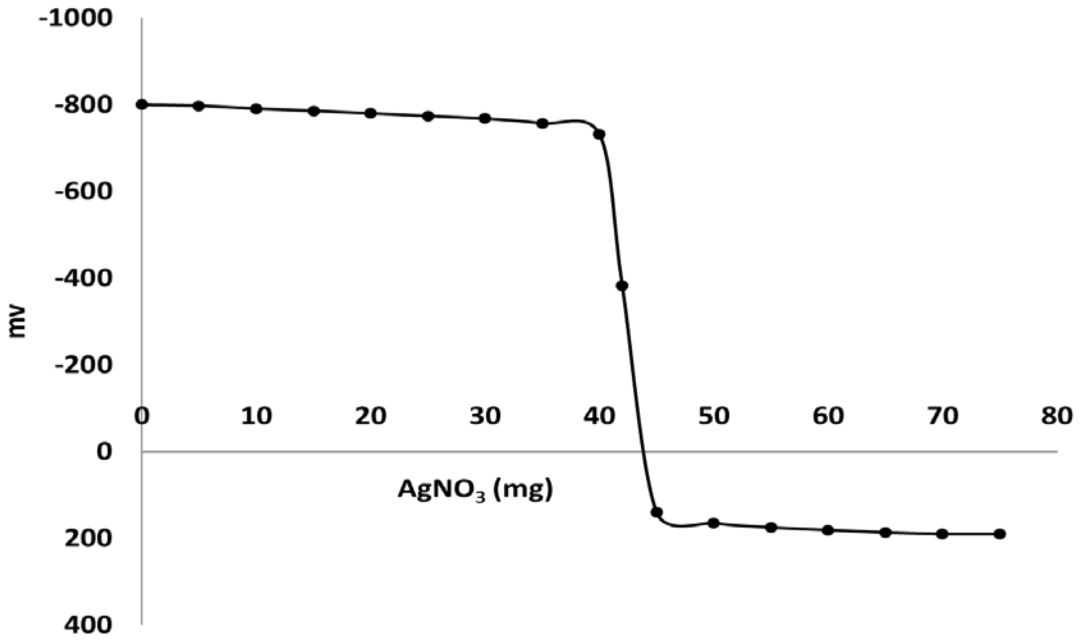

Figure 5.6: Titration of 4.5 mg of Na_2S with 1g L^{-1} $AgNO_3$ solution

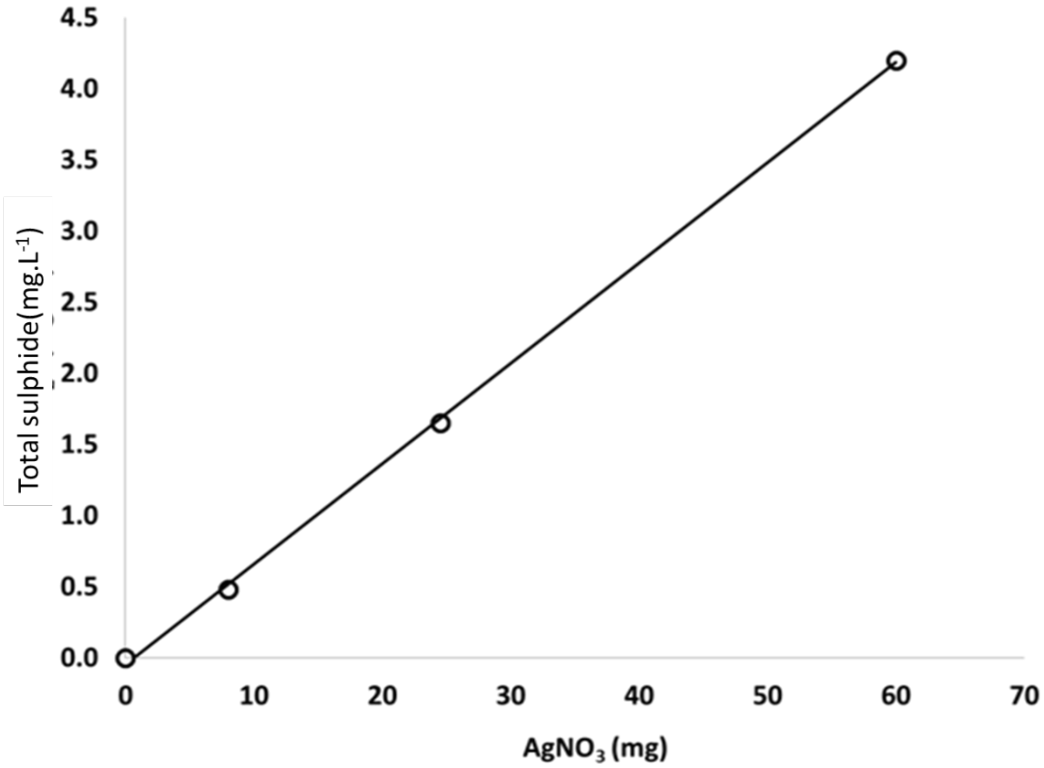

Figure 5.7: Calibration curve developed using $AgNO_3$ titration readings

5.4 Addition of optimum amount of iron salt to control H_2S

Observation of $AgNO_3$ titration showed the impact of the catalytic amount of Fe^{2+} (1mg/L) in Na_2S 5mg S/L containing solution at pH 8.3 (Figure 5.8). The presence of $Fe^{2+}$when it is compared with the controlling experiment (without Fe^{2+}) reduced the amount of sulfide by approximately by 50%. This experiment a provides good evidence that S^{2-} ion has been converted into some other form of sulfur in the presence of air and the catalytic amount of Fe^{2+}.

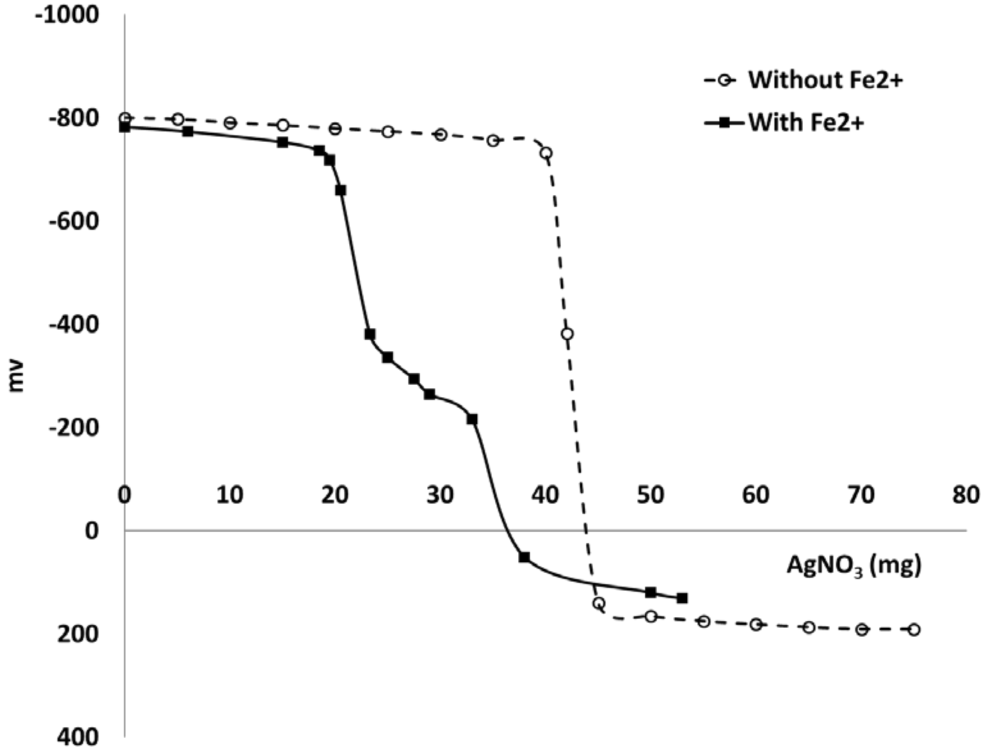

Figure 5.8: Titration of Na_2S with 1g L^{-1} $AgNO_3$ solution with and without ferrous iron

Further, titration result shows the similarities of the reactor water and Na_2S solution in the presence of the catalytic amount of Fe^{2+} iron (Figure 5.9). In both cases, there is a reduction of H_2S concentration and appearance of a “new” compound approximately at -300 mV. It should be noted that the usual methylene blue method measures 3.5 mg/L despite the actual results of H_2S being 2.5 mg/L. The titration result could be applied to identify the amount of HS which remains after the oxidation of H_2S in the sewer when a small amount of $Fe^{2+}$and air present at pH 8.2-8.5.

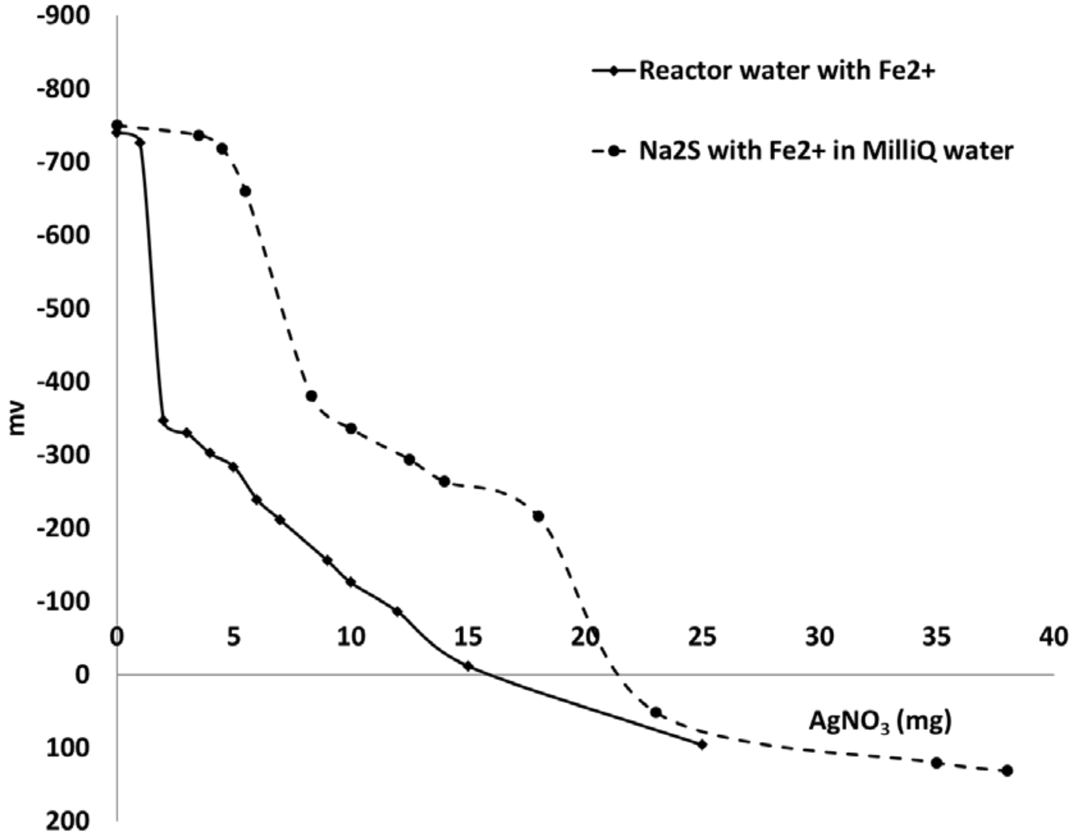

Figure 5.9: Titration of reactor water and N_2S solution with 1g L^{-1} $AgNO_3$ solution in the presence of Fe^{2+} ion

Chapter 6 : Model Development

6.1 Importance of the model development

If a model can simulate the sewer system after implementing the proposed sulfide mitigation method, a significant advantage could be achieved. Some of the major advantages are:

- The downstream changes of H_2S concentration in both liquid and the gaseous phases depending on the sewer conditions can be predicted.
- In some cases, the changes can be predicted under the conditions which are hard to implement in the laboratory environments.
- The most critical places that could be subjected to the sewer corrosion can be predicted.
- The most suitable places to implement sulfide mitigation methods could be identified.
- The ideal amount of chemicals required to reduce the sewer corrosion could be estimated.

6.2 Model development

According to the experimental results described in Chapter 5 and findings of the previous studies, following factors are identified as the main considerations for the model development.

- Sulfide concentration
- Oxygen concentration
- pH

- Temperature
- Amount of catalysts ($FeCl_2$) added into the system

Possible reactions of sulfide with oxygen are listed in Table 6.1. According to the previous studies and the outcomes of Chapter 4, the final product of the reaction between sulfide and oxygen depends on the initial reaction rate of the reactions.

Table 6.1: Possible reactions of sulfide with oxygen

Reactions	Product	Oxygen requirement (mg O/ mg S)
$2H_2S + ½O_2 \rightarrow H_2O + HS\text{-}SH$	S-S	0.25
$H_2S + ½O_2 \rightarrow S + H_2O$	$S_{(s)}$	0.50
$2H_2S + 2O_2 \rightarrow H_2S_2O_3 + H_2O$	$S_2O_3^{2-}$	0.75
$H_2S + 3/2O_2 \rightarrow H_2SO_3$	SO_3^{2-}	1.50
$H_2S + 2O_2 \rightarrow H_2SO_4$	SO_4^{2-}	2.00

Reaction considered:

$$H_2S + xO_2 = \text{Sulphur products} \qquad [21]$$

where, x is the stoichiometric coefficient. It should be noted that the stoichiometric coefficient is same as mg O_2/ mg S in Table 6.1 since atomic weight of S (32) and molecular weight of O_2 are same.

Reaction rate of H_2S reduction was expressed as:

$$\frac{dC_{H_2S}}{dt} = k_{H_2S} \bullet C_{H_2S} * C_{Fe} * C_O \bullet k_{pH} \qquad [22]$$

where,

k_{H_2S} = H_2S decay coefficient

C_{H_2S} = concentration of H_2S in liquid

C_{Fe} = concentration of $FeCl_2$

C_O = DO concertation

$k_{pH} = 10^{(-pH+7.5)*n}$

n = pH sensitivity coefficient

The experiment was done using Milli-Q water and Na_2S by adding two different quantities of catalyst (1 mg/L, 2 mg/L of $FeCl_2$). DO concentration was monitored with time. The pH was adjusted to 8.2 using $CaCO_3$ buffer solution. Initial DO and sulfide concentrations were 7.85 mg/L and 2 mg/L, respectively. Model prediction values fitted well with the measured DO values (Figure 6.1) when x was set to 0.75 (i.e. 0.75 mg O/mg S). while the mixture of many compounds is possible, the x value more matches with thiosulphate production.

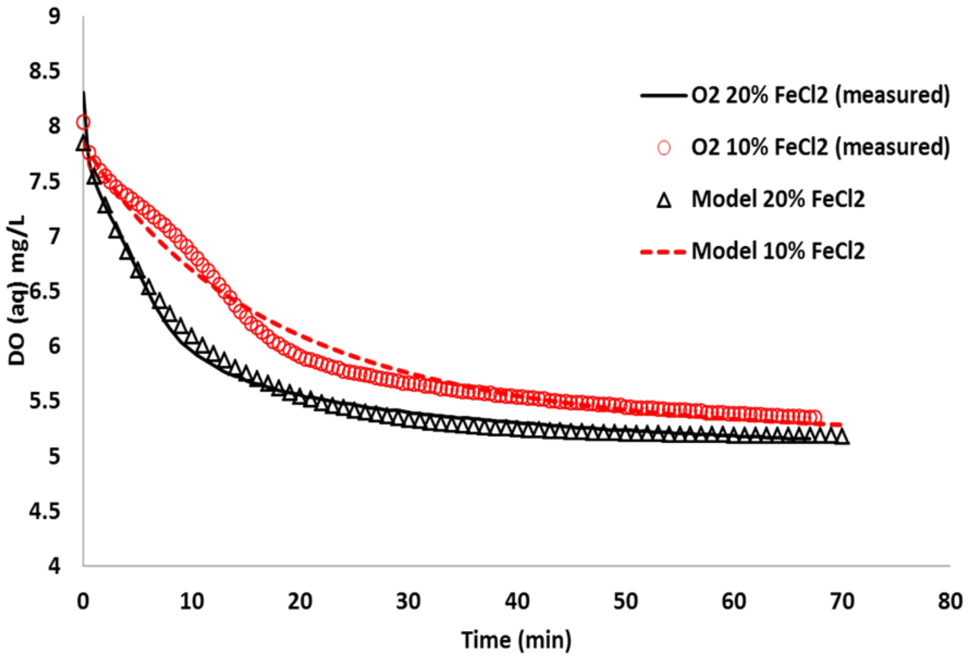

Figure 6.1: Model output vs. experimental results: DO reduction due to the reaction of sulfide with different $FeCl_2$ concentrations at pH 8.1 (initial DO: 7.85mg/L)

In the second set of the experiment, sulfide and DO concentrations were monitored with time and the model output is shown in Figure 6.2. In this experimental set again, stoichiometric coefficient, x of 0.75mg O_2/mg S, fitted the experimental data well. The x value is closer to that of thiosulphate. Used parameters and conditions are given in Table 6.2.

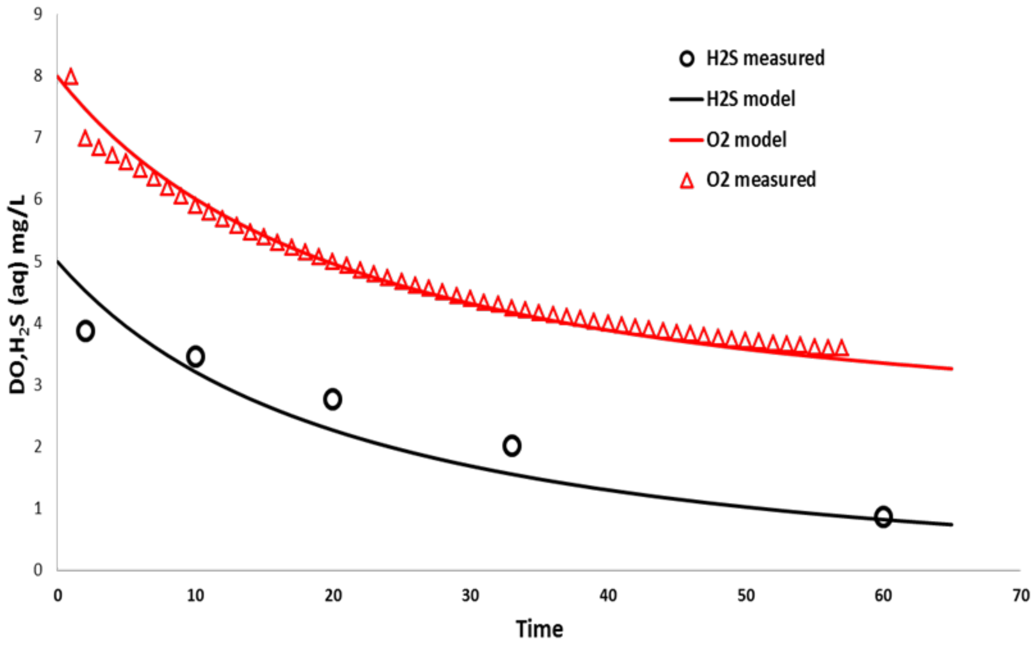

Figure 6.2: Model output vs. the experimental results: DO reaction with sulfide in the presence of 1mg/L $FeCl_2$ (initial DO: 7.85mg/L) at pH 7.8

In actual sewer systems, 7-8 mg/L DO concentration cannot be expected. DO concentrations in the real sewer system is about 1 mg/L. Another set of experiments were conducted using reactor water. Initial DO and sulfide concentrations were 1.5 mg/L and10 mg/L, respectively. In this situation, x had to be adjusted to 0.5 mg O_2/mg S to fit assuming the formed product is elemental sulfur, and it fitted well. Figure 6.3 shows the model output. Used parameters and conditions were given in Table 6.2.

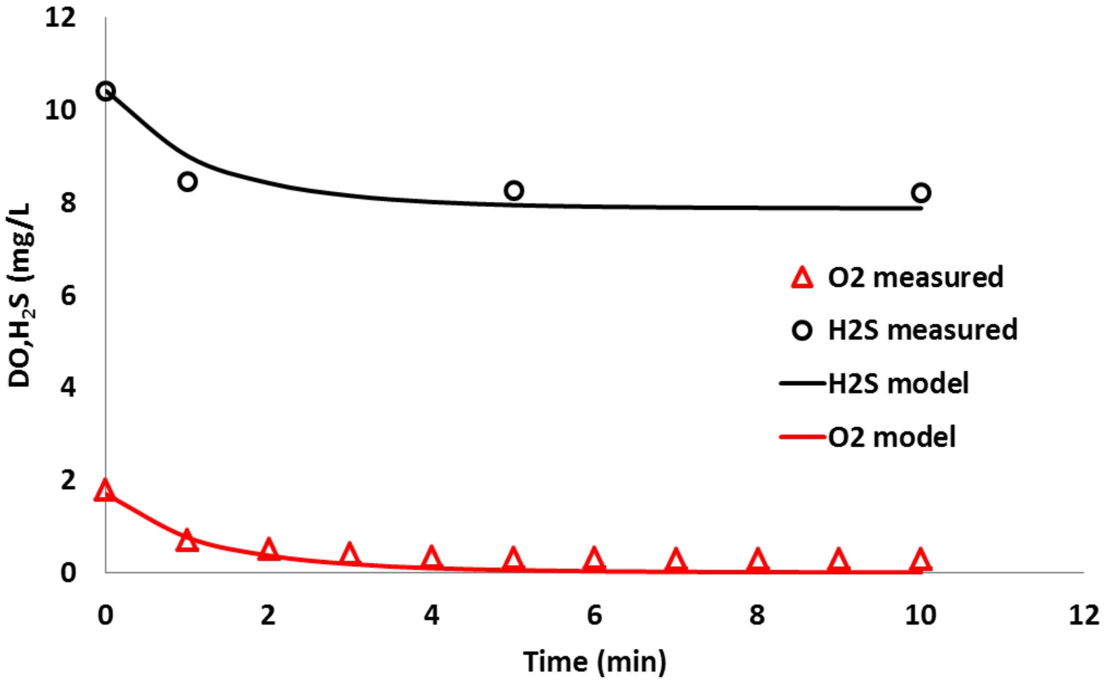

Figure 6.3: Model output: Oxygen reaction with sulfide in the reactor water in the presence of 1mg/l $FeCl_2$ assuming formed product is elemental sulfur

In the real sewer, sulfide concentration in the liquid phase is expected to be 1-2 mg/L. Hence, next experiment was conducted by diluting reactor water using nitrogen bubbled Milli-Q water. DO concentration and dissolved sulfide concentration was 1.5 mg/L and 1.2 mg/L respectively in the diluted water. $FeCl_2$ (1mg/L) was added to catalyze the reaction. In this situation, DO reduction rate was adjusted to 0.25 mg O_2/1 mg S to obtain a well-fitted model with measured DO and dissolved sulfide values. According to Table 6.1, the expected product of the reaction is disulfide. Figure 6.4 shows the comparison with model output. Used parameters and conditions were given in Table 6.2.

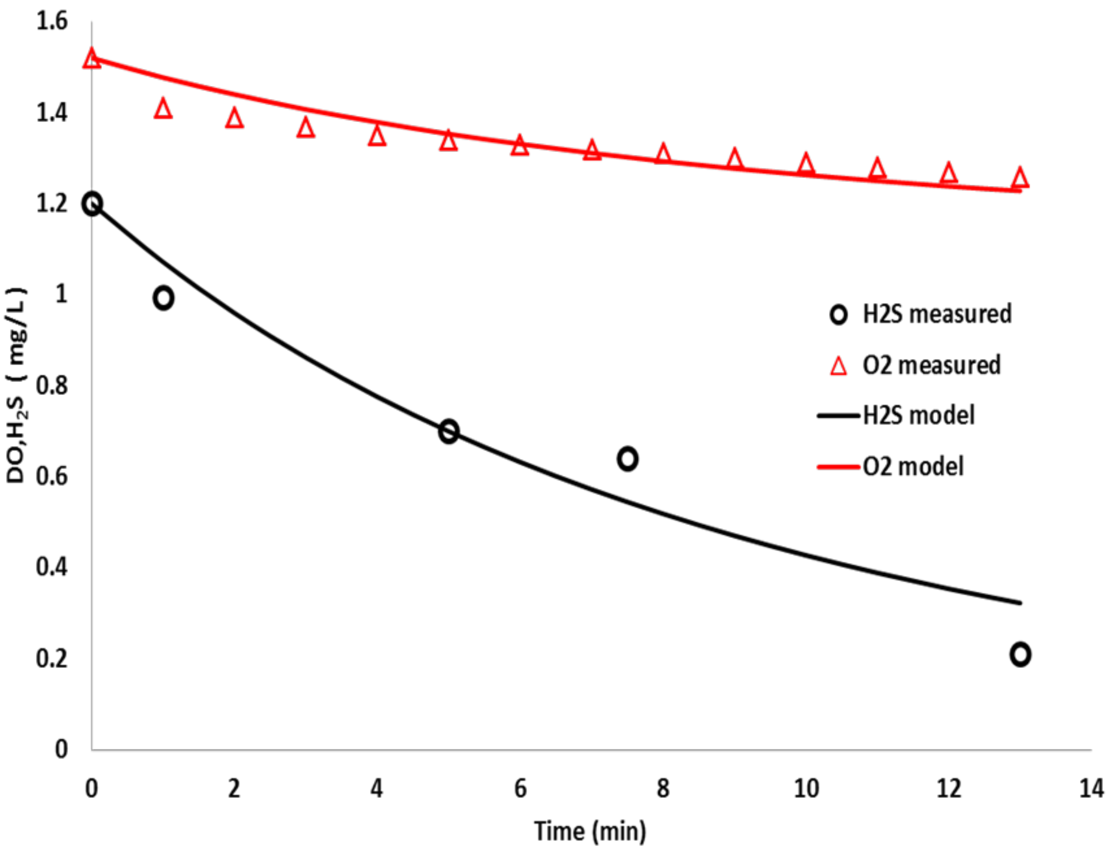

Figure 6.4: Model output: DO reaction with sulfide in reactor water in the presence of 1mg/L $FeCl_2$ assuming formed product is disulfide

Particularly in higher temperatures, DO concentration is very low in the real sewer system. If this new technology produces disulfide as the end product, it will be more cost-effective to implement in the real sewer system as it requires less amount of oxygen compared to other reactions (Table 6.1). Using experimental result k_{H_2S} and n (Equation 22) was estimated.

The model was developed to determine the oxygen requirement for the continuous sewer line using described experimental results and model parameters. Assumptions made for the development of the model for the continuous sewer line are:

- To remove 1 mg/L of sulfide required 0.25 mg/L oxygen (according to Table 6.1 oxygen required for the formation disulfide is only 0.25 mg/L)
- Sulfide production rate in the liquid phase of the sewer is 1 mg/L/h
- Initial DO concentration is 1 mg/L
- Initial dissolved sulfide concentration is 1 mg/L

Considering the above assumptions, output of the developed model is shown in Figure 6.5. Used parameters and conditions were given in Table 6.2.

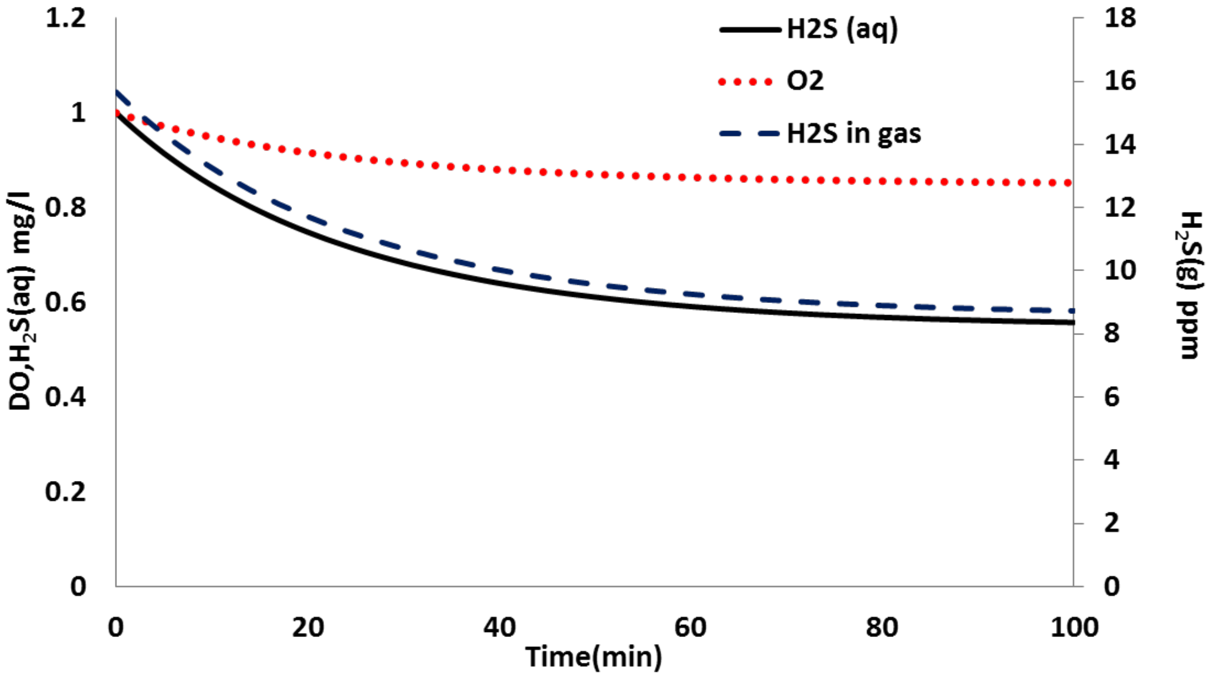

Figure 6.5: Model output for the sewer line with the continuous sulfide production of 1 mg/L/h with the time

In the model, the required DO and $FeCl_2$ was adjusted to keep H_2S concentration below 10 ppm in the gaseous phase – widely adopted guideline by the utilities. The pH was adjusted to 8.2. According to the model, if $FeCl_2$ can be maintained above 1 mg/L all the time, the required amount of DO to keep the gaseous phase H_2S concentration below 10 ppm is 0.33 mg/L/h. Depending on temperature and microbial utilisation of BOD the DO requirement can change, but this needs further experimentation to confirm.

Table 6.2: Conditions and parameters used for the modeling

Referring figure	Figure 6.2	Figure 6.3	Figure 6.4 & 6.5
Initial H_2S (mg/L)	5	10.4	1.2
Initial DO (mg/L)	8	1.69	1.52
Initial $FeCl_2$ (mg/L)	2	2	1
pH	8.0	8.2	8.2
k_{H_2S}	0.1	0.1	0.1
n	2.5	0.75	0.75
x (mg O_2/ mg S)	0.75	0.50	0.25
Assumed product	$S_2O_3^{2-}$	S_0	H_2S_2

6.3 Summary of the observation

Table 6.3: Suspected sulfur compounds and required conditions could be formed in the sewer after the catalytic reaction with O_2 (with the presence of 1-2mg/L $FeCl_2$)

Suspected sulfur compound	Required DO level (mg/L)	H_2S Level in liquid (mg/L)	pH	Possibility to be reprocessed by bacteria
SO_4^{3-}	8-9	>5	<7.6	SRB can consume and produce H_2S again.
$S_2O_3^{2-}$	8-9	>5	7.8-8.1	It will be oxidized to SO_4^{2-} easily with the time.

S_0	1.5-2	>5	8.0-8.2	SRB will not consume
H_2S_2	1-1.5	<5	8.1-8.3	SRB will not consume

Chapter 7 : Conclusion and Recommendations

7.1 Conclusion

A significant progress on understanding of generation and control of H_2S in the gas phase in a sewer was achieved by:

1. Designing and commissioning of a laboratory reactor to simulate H_2S production and evaluate corrosion control methods,
2. Identification of a mechanism which reduces H_2S concentration in a gas phase more than the supposed equilibrium based on the liquid H_2S concentration and pH,
3. Identification of the catalytical effect of Fe^{2+} on oxidation of H_2S,
4. Proving that pH elevation from 7.6 to 8 produces a dual effect on H_2S gas concentration, i.e., shifts H_2S equilibrium and enables more efficient oxidation of H_2S in addition to known inhibitory effect on microbes to reduce H_2S concentration.
5. The possible sulfur product was identified after the catalytic reaction of dissolved sulfide with different concentrations of oxygen levels.
6. The model was developed using experimental results.
7. Table 7.1 demonstrates the multiple benefits of the proposed method over the existing practices.

Table 7.1: Comparison of proposed controlling method with the existing methods

Existing Method	Disadvantage of existing methods	Advantage of proposed method
Addition of $FeCl_3$ / $FeCl_2$	- Required large amount of chemical, - Not cost effective, 10.9 - 170.6 \$/ML (Ganigue et al. 2011) - Difficult to treat in the downstream formation of a large amount of sludge.	- Reduces 90% current requirements of ferrous, - Cost will be roughly 10-20% of $FeCl_3$ addition cost. - Easy to treat in downstream.
Addition of O_2	- Required large amount of O_2., - Not cost effective, 12.8 - 74.0 \$/ML(Ganigue et al. 2011) - The most cases final product is SO_4^{2-} which can be converted into H_2S by SRB.	- The required amount of O_2 is very low; most of the time, DO level in the sewer system is enough. - The final product (S_0 / H_2S_2) could not be converted to H_2S easily by microbes.
Adjusting pH	- Required to adjust pH > 9.5 to eliminate H_2S in the gas phase. - Chemical (NaOH / $Mg(OH)_2$) requirement is very high. - Not cost effective. 39.6 - 99.1 \$/ML and 48.7 - 159.3 \$/ML for NaOH and $Mg(OH)_2$ respectively (Ganigue et al. 2011).	- A slight adjustment of pH is enough (from 7.6 to 8.2-8.3) - Recommended to use $Ca(OH)_2$ which is cheaply available comparing with other metal hydroxides.

	- Difficult to treat in downstream.	

The findings reported in this research are original and so far not reported. Based on these findings, it can be concluded that mechanisms for hydrogen sulfide reduction in headspace in gravity sewers where significant corrosion is prevalent, is more effective. It is anticipated that developed laboratory setting of control strategy will be verified on a live system in future research.

7.2 Recommendations for future research

- The detailed mechanisms behind the proposed new method need to be explored further especially after the appropriate development of methods for sulfur species.
- It is interesting to implement proposed method in actual gravity sewer system.
- The model needs to be checked with the data collected from the actual sewer system, and further, it requires modification by adding other effecting parameters in the real sewer system.

Chapter 8 : Reference

Abdikheibari, S, Song, H-m, Cho, J-i, Kim, S-j, Gwon, S-c, Park, K, Maluleque, B, Marleni, N, Shu, L & Jegatheesan, V 2016, 'In-situ evaluation of predictive models for H 2 S gas emission and the performance of optimal dosage of suppressing chemicals in a laboratory-scale sewer', *International Biodeterioration & Biodegradation*, vol. 106, pp. 25-33.

Al Zuhair, S, El-Naas, MH & Al Hassani, H 2008, 'Sulfate inhibition effect on sulfate reducing bacteria', *Journal of Biochemical Technology*, vol. 1, no. 2, pp. 39-44.

Araújo, A, De Oliveira, R, Mara, D, Pearson, H & Silva, S 2000, 'Sulphur and phosphorus transformations in wastewater storage and treatment reservoirs in northeast Brazil', *Water science and technology*, vol. 42, no. 10-11, pp. 203-10.

Baumgartner, LK, Reid, RP, Dupraz, C, Decho, AW, Buckley, DH, Spear, JR, Przekop, KM & Visscher, PT 2006, 'Sulfate reducing bacteria in microbial mats: Changing paradigms, new discoveries', *Sedimentary Geology*, vol. 185, no. 3–4, pp. 131-45.

Boon, AG 1995, 'Septicity in sewers: Causes, consequences and containment', *Water Science and Technology*, vol. 31, no. 7, pp. 237-53.

Brongers, M 2002, 'Appendix K. Drinking water and sewer systems in corrosion costs and preventative strategies in the United States', *Rep. FHWA-RD-01*, vol. 156.

Cadena, F & Peters, RW 1988, 'Evaluation of chemical oxidizers for hydrogen sulfide control', *Journal (Water Pollution Control Federation)*, pp. 1259-63.

Chen, KY & Morris, JC 1972, 'Kinetics of oxidation of aqueous sulfide by oxygen', *Environmental Science & Technology*, vol. 6, no. 6, pp. 529-37.

Churchill, P & Elmer, D 1999, 'Hydrogen sulfide odor control in wastewater collection systems', *J NEW ENGL WATER ENVIRON ASSOC*, vol. 33, no. 1, pp. 57-63.

De Lomas, JG, Corzo, A, Gonzalez, JM, Andrades, JA, Iglesias, E & Montero, MJ 2006, 'Nitrate promotes biological oxidation of sulfide in wastewaters: experiment at plant-scale', *Biotechnol. Bioeng*, vol. 93, no. 4, pp. 801-11.

Delgado, S, Alvarez, M, Rodriguez-gomez, LE & Aguiar, E 1999, 'H2S generation in a reclaimed urban wastewater pipe. case study: Tenerife (Spain)', *Water Research*, vol. 33, no. 2, pp. 539-47.

Firer, D, Friedler, E & Lahav, O 2008, 'Control of sulfide in sewer systems by dosage of iron salts: comparison between theoretical and experimental results, and practical implications', *Science of the total environment*, vol. 392, no. 1, pp. 145-56.

Ganigue, R, Gutierrez, O, Rootsey, R & Yuan, Z 2011, 'Chemical dosing for sulfide control in Australia: an industry survey', *Water Research*, vol. 45, no. 19, pp. 6564-74.

Gudjonsson, G, Vollertsen, J & Hvitved-Jacobsen, T 2002, 'Dissolved oxygen in gravity sewers–measurement and simulation', *Water science and technology*, vol. 45, no. 3, pp. 35-44.

Gutierrez, O, Mohanakrishnan, J, Sharma, KR, Meyer, RL, Keller, J & Yuan, Z 2008, 'Evaluation of oxygen injection as a means of controlling sulfide production in a sewer system', *Water research*, vol. 42, no. 17, pp. 4549-61.

Haveman, SA, Greene, EA & Voordouw, G 2005, 'Gene expression analysis of the mechanism of inhibition of Desulfovibrio vulgaris Hildenborough by nitrate-reducing, sulfide-oxidizing bacteria', *Environmental microbiology*, vol. 7, no. 9, pp. 1461-5.

Henze, M 1997, 'Trends in advanced wastewater treatment', *Water Science and Technology*, vol. 35, no. 10, pp. 1-4.

Hvitved-Jacobsen, T, Raunkjær, K & Nielsen, PH 1995, 'Volatile fatty acids and sulfide in pressure mains', *Water Science and Technology*, vol. 31, no. 7, pp. 169-79.

Hvitved-Jacobsen, T, Vollertsen, J & Nielsen, AH 2013, *Sewer processes: microbial and chemical process engineering of sewer networks*, CRC press.

Jameel, P 1989, 'The use of ferrous chloride to control dissolved sulfides in interceptor sewers', *Journal (Water Pollution Control Federation)*, pp. 230-6.

Jegatheesan, V, Abdikheibari, S, Marleni, N, Phelan, S, Park, K, Bagshaw, S, Farago, L & Shu, L 2015, 'Estimating hydrogen sulphide dissipation rate constant under the influence of different chemical dosing', *International Biodeterioration & Biodegradation*, vol. 101, pp. 47-55.

Jiang, G, Sharma, KR, Guisasola, A, Keller, J & Yuan, Z 2009, 'Sulfur transformation in rising main sewers receiving nitrate dosage', *Water research*, vol. 43, no. 17, pp. 4430-40.

Keller-Lehmann, B, Corrie, S, Ravn, R, Yuan, Z & Keller, J 2006, 'Preservation and simultaneous analysis of relevant soluble sulfur species in sewage samples', in *Proceedings of the Second International IWA Conference on Sewer Operation and Maintenance*, vol. 26, p. 28.

Lahav, O, Sagiv, A & Friedler, E 2006, 'A different approach for predicting H 2 S (g) emission rates in gravity sewers', *Water research*, vol. 40, no. 2, pp. 259-66.

Mohanakrishnan, J 2008, 'Role of anaerobic biofilm in sewer biotransformations'.

Moosa, S, Nemati, M & Harrison, S 2002, 'A kinetic study on anaerobic reduction of sulphate, Part I: Effect of sulphate concentration', *Chemical Engineering Science*, vol. 57, no. 14, pp. 2773-80.

Moosa, S, Nemati, M & Harrison, ST 2005, 'A kinetic study on anaerobic reduction of sulphate, part II: incorporation of temperature effects in the kinetic model', *Chemical Engineering Science*, vol. 60, no. 13, pp. 3517-24.

Moosa, S, Nemati, M & Harrison, STL 2005, 'A kinetic study on anaerobic reduction of sulphate, part II: incorporation of temperature effects in the kinetic model', *Chemical Engineering Science*, vol. 60, no. 13, pp. 3517-24.

Mori, T, Nonaka, T, Tazaki, K, Koga, M, Hikosaka, Y & Noda, S 1992, 'Interactions of nutrients, moisture and pH on microbial corrosion of concrete sewer pipes', *Water Research*, vol. 26, no. 1, pp. 29-37.

Muyzer, G & Stams, AJ 2008, 'The ecology and biotechnology of sulphate-reducing bacteria', *Nature Reviews Microbiology*, vol. 6, no. 6, pp. 441-54.

Nielsen, AH, Lens, P, Vollertsen, J & Hvitved-Jacobsen, T 2005, 'Sulfide–iron interactions in domestic wastewater from a gravity sewer', *Water research*, vol. 39, no. 12, pp. 2747-55.

Nielsen, AH, Vollertsen, J & Hvitved-Jacobsen, T 2003, 'Determination of kinetics and stoichiometry of chemical sulfide oxidation in wastewater of sewer networks', *Environmental science & technology*, vol. 37, no. 17, pp. 3853-8.

Nielsen, AH, Vollertsen, J, Jensen, HS, Wium-Andersen, T & Hvitved-Jacobsen, T 2008, 'Influence of pipe material and surfaces on sulfide related odor and corrosion in sewers', *Water Research*, vol. 42, no. 15, pp. 4206-14.

Nielsen, PH, Raunkjær, K & Hvitved-Jacobsen, T 1998, 'Sulfide production and wastewater quality in pressure mains', *Water Science and Technology*, vol. 37, no. 1, pp. 97-104.

Norsker, NH, Nielsen, PH & Hvitved-Jacobsen, T 1995, 'Influence of oxygen on biofilm growth and potential sulfate reduction in gravity sewer biofilm', *Water Science and Technology*, vol. 31, no. 7, pp. 159-67.

Padival, NA, Kimbell, WA & Redner, JA 1995, 'Use of iron salts to control dissolved sulfide in trunk sewers', *Journal of Environmental Engineering*, vol. 121, no. 11, pp. 824-9.

Park, K, Lee, H, Phelan, S, Liyanaarachchi, S, Marleni, N, Navaratna, D, Jegatheesan, V & Shu, L 2014a, 'Mitigation strategies of hydrogen sulphide emission in sewer networks–a review', *International Biodeterioration & Biodegradation*, vol. 95, pp. 251-61.

—— 2014b, 'Mitigation strategies of hydrogen sulphide emission in sewer networks – A review', *International Biodeterioration & Biodegradation*, vol. 95, Part A, pp. 251-61.

Roberts, DJ, Nica, D, Zuo, G & Davis, JL 2002, 'Quantifying microbially induced deterioration of concrete: initial studies', *International Biodeterioration & Biodegradation*, vol. 49, no. 4, pp. 227-34.

Rodríguez-Gómez, LE, Delgado, S, Álvarez, M & Elmaleh, S 2005, 'Inhibition of sulfide generation in a reclaimed wastewater pipe by nitrate dosage and denitrification kinetics', *Water Environment Research*, vol. 77, no. 2, pp. 193-8.

Santry, I 1963, 'Hydrogen sulfide in sewers', *Journal (Water Pollution Control Federation)*, pp. 1580-8.

Sharma, K, Derlon, N, Hu, S & Yuan, Z 2014, 'Modeling the pH effect on sulfidogenesis in anaerobic sewer biofilm', *Water research*, vol. 49, pp. 175-85.

Sharma, K, Ganigue, R & Yuan, Z 2013, 'pH dynamics in sewers and its modeling', *Water Research*, vol. 47, no. 16, pp. 6086-96.

Takeno, N 2005, 'Atlas of Eh-pH diagrams'.

Thistlethwayte, DKB 1972, *Control of sulphides in sewerage systems*, Ann Arbor Science.

Tomar, M & Abdullah, THA 1994, 'Evaluation of chemicals to control the generation of malodorous hydrogen sulfide in waste water', *Water Research*, vol. 28, no. 12, pp. 2545-52.

Transfer, USEPAOoT & Pomeroy, RD 1974, *Process design manual for sulfide control in sanitary sewerage systems*.

Yongsiri, C, Vollertsen, J & Hvitved-Jacobsen, T 2002, 'Air-water transfer of hydrogen sulfide-an approach for application in sewer networks', *Proceedings of the Water Environment Federation*, vol. 2002, no. 5, pp. 109-22.

—— 2004, 'Effect of temperature on air-water transfer of hydrogen sulfide', *Journal of Environmental Engineering*, vol. 130, no. 1, pp. 104-9.

—— 2005, 'Influence of wastewater constituents on hydrogen sulfide emission in sewer networks', *Journal of Environmental Engineering*, vol. 131, no. 12, pp. 1676-83.

Yongsiri, C, Vollertsen, J, Rasmussen, M & Hvitved–Jacobsen, T 2004, 'Air–water transfer of hydrogen sulfide: an approach for application in sewer networks', *Water Environment Research*, vol. 76, no. 1, pp. 81-8.

Zhang, L, De Schryver, P, De Gusseme, B, De Muynck, W, Boon, N & Verstraete, W 2008, 'Chemical and biological technologies for hydrogen sulfide emission control in sewer systems: a review', *Water research*, vol. 42, no. 1, pp. 1-12.

Zhang, L, Keller, J & Yuan, Z 2009, 'Inhibition of sulfate-reducing and methanogenic activities of anaerobic sewer biofilms by ferric iron dosing', *Water Research*, vol. 43, no. 17, pp. 4123-32.