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Evaluation of a combined treatment to control gaseous phase H_2S in sewer

Dileepa Rathnayake, George Kastl, Arumugam Sathasivan*

School of Computing Engineering and Mathematics, Western Sydney University, Kingswood, NSW, 2747, Australia

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A B S T R A C T

Hydrogen sulphide (H_2S) generation in sewer systems is a serious problem. A cost effective means of controlling sewer corrosion has been tested in a laboratory scale sewer model which includes a concrete surface. Traditionally two most practised methods are pH adjusted to >10.5 and ferrous chloride addition at $[Fe^{2+}]$: $[S^{2-}]$ of 1–1.3:1. When the combined methods were tested in a laboratory scale sewer system, the amount of ferrous chloride required was only at $[Fe^{2+}]$: $[S^{2-}]$ of 0.1:1 and pH~8. Further experiments confirmed some oxygen in the water/air space is necessary to achieve an efficient reduction, but the oxygen present in the water (~1 mg/L) of gravity sewer was found sufficient. This provides a cost-effective means of H_2S reduction in the gaseous phase, although testing with real sewer is needed.

1. Introduction

The production of hydrogen sulphide (H_2S) is a serious problem in sewer systems due to the sensory unpleasantness, toxicity and corrosion of sewer infrastructure (Boon, 1995; Nielsen et al., 2008; Zhang et al., 2008). Sewer pipes subjected to hydrogen sulphide atmosphere can potentially exhibit structural failure and collapse 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 cause of H_2S generation is biogenic. Sulphate in the sewer is reduced to sulphide by sulphate reducing bacteria (SRB). SRB reduce sulphate while oxidizing organic carbon in anaerobic sewers (Baumgartner et al., 2006). A part of the H_2S from the aqueous phase of sewers is emitted into the atmospheric space 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).

$$H_2S+2O_2 \rightarrow H_2SO_4 \tag{1}$$

The concentration of H_2S in wastewater is determined by production rates, emissions into the atmosphere and oxidation of H_2S by oxygen entering from the atmosphere through manholes and cracks.

The rate of sulphide production is influenced by factors such as 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 provide an ideal environment for H_2S production as it is always submerged in flowing water containing high biochemical oxygen demand (BOD) and a limited amount of oxygen (Firer et al., 2008). In an anaerobic environment, in the presence of sulfate, methanogenic bacteria compete with SRB for the accessible substrates. The end result of this competition is important as it will determine to what extent sulphide and methane will be produced (Acharya et al., 2008). The competition between SRB and MPB in consumption depends mainly on the forms of substrates and COD/sulphate ratio (Li et al., 1996). SRB can utilize low molecular weight organic compounds such as acetate, ethanol methanol, butyrate propionate and, lactate (Nagpal et al., 2000).

Emission of H_2S into the gas phase is widely reported to be mainly controlled by the total dissolved sulphide concentration, the pH in the liquid phase, temperature and the hydraulic properties of

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* Corresponding author.
E-mail addresses: Dileepa.Rathnayake@westernsydeny.edu.au (D. Rathnayake), george.kastl@gmail.com (G. Kastl), s.sathasivan@westernsydeny.edu.au (A. Sathasivan).

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the sewer network (Ganigue et al., 2011; Yongsiri et al., 2004). Sulphide can exist in water as H_2S (aq), HS^{2-} (aq) and S^{2-} (aq) but only H_2S escapes water and causes corrosion (Lahav et al., 2006). The relative concentrations of H_2S (aq), HS^- and S^{2-} in the liquid are determined by pH, according to the following equilibrium relationship:

$$H_2S \leftarrow\rightarrow H^+ + HS^- \leftarrow\rightarrow S^{2-} + 2H^+ \quad (2)$$

Equilibrium considerations result in the following equations:

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

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

$$\mathrm{Log}\frac{[HS^-]}{[H_2S(aq)]} = \mathrm{pH} - \mathrm{pK}_{a,1} \quad (5)$$

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

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) for typical wastewater conditions.

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

$$H^{cp} = C_a/P \quad (7)$$

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

To solve this biogenic corrosion problem, several techniques have been considered. The leading methods adopted to date to moderate effects of H_2S control have been the dosage of chemicals to the wastewater. For each method, there is a great range of cost reported (Park et al., 2014), depending on conditions of the sewer and the environment the sewer is in.

The addition of metal hydroxides such as magnesium hydroxide ($Mg(OH)_2$), sodium hydroxide (NaOH) to raise the pH of the sewer, is used to reduce H_2S emission to the gaseous phase of the sewer systems (Hvitved-Jacobsen et al., 2013). $Mg(OH)_2$ increases the pH of wastewater up to a maximum value of 9.0, but the increase was gradual because of its low dissolution rate (Gutierrez et al., 2009). However, NaOH addition is a periodic "shock dosing" of wastewater to achieve a pH of 12.5–13 for a brief period (Park et al., 2014). According to the equilibrium considerations (Equations (2)–(6)), it is a necessity to increase pH more than 10.5 to increase S^{2-} portion to significantly reduce $H_2S_{(aq)}$.

Raising pH to 8.6–9.0 considerably reduces SRB activities of sewer biofilms and prevents escape into the gas phase. 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 (Gutierrez et al., 2009). Temperature is another significant factor, which affects the activity of SRB with a maximum H_2S production rate at 35 °C (Moosa et al., 2005).

The supply of air (or oxygen) to prevent anaerobic environments and to oxidize sulphide to sulphur has been used for control of H_2S production (Zhang et al., 2008). Further, the addition of nitrate (NO_3^-) to an anaerobic wastewater will form anoxic environments (De Lomas et al., 2006; Haveman et al., 2005), but nitrate is not capable of oxidizing dissolved sulphide to the same extent as oxygen (Hvitved-Jacobsen et al., 2013). Strong electron acceptors such as H_2O_2, NaOCl or $KMnO_4$ have also been used for the chemical sulphide oxidation (Tomar and Abdullah, 1994).

The addition of iron salts such as ferrous chloride and ferric chloride is the most commonly used method for H_2S control (Zhang et al., 2009). Iron does not prevent the formation of H_2S, but binds sulphide preventing its transfer into the gas phase. There are some contradictions about the effectiveness of the iron salt. According to Jameel (1989), ferrous chloride is more than two times effective in controlling the dissolved sulphide concentration than ferric chloride. However, in another report (Tomar and Abdullah, 1994), ferric chloride was found to be more effective than ferrous chloride. It is reported that addition of ferric ions reduced the sulphate reduction and methane production rates of the sewer biofilms by 60% and 80%, respectively (Zhang et al., 2009). Ferrous iron (Fe^{2+}) forms ferrous sulphide (FeS) to remove soluble sulphide irons by precipitation (Nielsen et al., 2005).

$$Fe^{2+}_{(aq)} + HS^-_{(aq)} \rightarrow FeS_{(s)} + H^+_{(aq)} \quad (8)$$

Ferric iron (Fe^{3+}) oxidizes sulphide to elemental sulphur (S_o), and the oxidizing reaction forms Fe^{2+} which removes dissolved sulphide by forming FeS, but the reaction of Fe^{3+} is considerably slower than Fe^{2+} (Hvitved-Jacobsen et al., 2013).

$$2Fe^{3+}_{(aq)} + HS^-_{(aq)} \rightarrow 2Fe^{2+}_{(aq)} + S_{o(s)} + H^+_{(aq)} \quad (9)$$

Padival et al., claim that combination of ferrous and ferric salts is more effective for sulphide removal in comparison with either salt alone (Padival et al., 1995). They reported that the reduction in the gaseous phase was not according to equilibrium (Equations (2)–(6))/precipitation (Equations (8) and (9)) when the reaction occurred at different pH values.

Further, it is reported that sulphide oxidation reaction is highly susceptible to catalysis and inhibition (Nielsen et al., 2003). A trace amount of metals is sufficient to increase the reaction rate considerably (Kuhn et al., 1983). All the tested metal ions catalyzed the oxidation process, and the organic substances possess either catalytic or inhibitory effect (Chen and Morris, 1972). They also reported the formation of polysulfide and the change in reaction rate with pH. They further found the stoichiometry also changes when the oxidation process was catalyzed (Chen and Morris, 1972). Therefore, a combination of pH adjustment and ferrous salt may provide a better scope in preventing the H_2S emission into the gaseous phase.

To do this, a reactor set representing the sewer was needed. In most previous experiments either gas phase measurements are not made (Firer et al., 2008; Mathioudakis et al., 2006) or when made they (reactors) were maintained airtight to represent the rising sewer (Jiang et al., 2009). In most cases, the total sulphide concentration in the liquid phase is used to calculate the atmospheric $H_2S(g)$ concentrations (Abdikheibari et al., 2016). In another model attempting to simulate the actual sewer, the sulphide dissipation rate constant was recently predicted for several dosed chemicals to decrease H_2S concentration in the liquid phase (Jegatheesan et al., 2015). But in both cases, the calculated $H_2S_{(g)}$ concentrations were not compared with the measured gaseous phase H_2S concentrations.

Ferric chloride dosing, pH adjustment and air (oxygen) dosing were commonly used as the sewer corrosion control methods, but individual methods were expensive and has serious consequences such as the added ferrous chloride causing sludge treatment and disposal issues (Jameel, 1989; Padival et al., 1995; Poulton et al.,