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Estimating hydrogen sulphide dissipation rate constant under the influence of different chemical dosing



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ABSTRACT

Sewer odour and corrosion is caused by the reduction of sulphide ions and the release of hydrogen sulphide gas (H₂S) into the sewer atmosphere. The reduction of sulphide is determined by its dissipation rate which depends on many processes such as emission, oxidation and precipitation that prevail in wastewater environments. Two factors that mainly affect the dissipation of sulphide are sewer hydraulics and wastewater characteristics; modification to the latter by dosing certain chemicals is known as one of the mitigation strategies to control the dissipation of sulphide. This study investigates the dissipation of sulphide in the presence of NaOH, Mg(OH)₂, Ca(NO₃)₂ and FeCl₃ and the dissipation rate is developed as a function of hydraulic parameters such as the slope of the sewer and the velocity gradient. Experiments were conducted in a 18 m experimental sewer pipe with adjustable slope to which, firstly no chemical was added and secondly each of the above mentioned chemicals was supplemented in turn. A dissipation rate constant of 2×10^{-6} for sulphide was obtained from experiments with no chemical addition. This value was then used to predict the sulphide concentration that was responsible for the emission of H₂S gas in the presence of one of the above mentioned four chemicals. It was found that the performance of alkali substances (NaOH and Mg(OH)₂) in suppressing the H₂S gas emission was excellent while ferric chloride showed a moderate mitigating effect due to its slow reaction kinetics. Calcium nitrate was of little value since the wastewater used in this study experienced almost no biological growth. Thus the effectiveness of selected chemicals in suppressing H₂S gas emission had the following order: NaOH > Mg(OH)₂ > FeCl₃ > Ca(NO₃)₂.

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Introduction

Hydrogen sulphide (H₂S) is a naturally occurring gas in many sewer systems, which possesses various deteriorating characteristics such as flammability, explosivity, toxicity and corrosivity. According to water authorities, obnoxious odour, corrosion and health problems are among the unfavourable proceedings of the emission of hydrogen sulphide. Sewer gas seeping from drains has potential to create a toxic environment that imposes health hazards to the community that could range from breathing difficulties and irritation in eyes and skin to fatality. Furthermore, the problematic

effect of hydrogen sulphide can be most challenging to sewer networks as it can corrode sewers as well as lift stations comprised of metallic or concrete pipes (United States Environmental Protection Agency, 1974; Nielsen et al., 2003; Hvitved-Jacobsen et al., 2013; Adgate et al., 2014).

Total sulphide in wastewater exists in three forms namely elemental sulphur, metal sulphide and dissolved sulphide. While the elemental sulphur and metal sulphides (which will generally be in the form of precipitates) will not be contributing to the generation of H₂S, the dissolved sulphide would. Dissolved sulphide is composed of three species which are hydrogen sulphide (H₂S), mono-hydrogen sulphide (HS⁻) and sulphide (S²⁻) and the combination of these three sulphide species is usually called as total dissolved sulphide in wastewater. Only hydrogen sulphide (H₂S) species can be further released to sewer atmosphere (Yongsiri et al., 2003). Sewer processes that relate to total sulphide content in wastewater involve four transformation processes: (i) generation of

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sulphide (ii) chemical and biological oxidation of sulphide (iii) emission of sulphide and (iv) precipitation of sulphide (Nielsen et al., 2008a). These processes depend on a range of factors including temperature, wastewater flow or residence time in the sewerage, type of sewer pipe (pressurised or gravity), sewerage structure (i.e. shape and slope), quality of wastewater and the nature of biochemical processes that occur in the bulk water and the biofilm or sediment that is attached to the inner wall of sewer pipes (Nielsen and Hvitved-Jacobsen, 1988; Nielsen et al., 1992, 2008b; Almeida et al., 1999; Tanaka et al., 2000). Out of those four transformation processes mentioned above, three of them dissipate the total dissolved sulphide from the wastewater through emission, oxidation and precipitation. Those processes occur simultaneously, particularly in gravity sewer pipes.

The favourable sulphide oxidation, leading to the mitigation of hydrogen sulphide gas, can occur chemically as well as biologically (Gutierrez et al., 2008). In natural or introduced aerobic conditions, when dissolved oxygen is present in the system, mono-hydrogen sulphide ions are oxidized to sulphate ions through a chain reaction. Nielsen et al. (2006) reported a chemical oxidation rate of $2.5 \text{ g of S m}^{-3} \text{ h}^{-1}$ in a sterilized wastewater. Buisman et al. (1990) reported a higher value for the oxidation rate (at $3.0 \text{ g of S m}^{-3} \text{ h}^{-1}$) in a phosphate buffered system. In both cases experiments were conducted at a typical sewer pH of 8.0 and a temperature of $25 \text{ }^\circ\text{C}$. In addition to the aforementioned process, dosing sewer with oxidizing agents including H_2O_2 , Cl_2 and KMnO_4 is a common practice to oxidize sulphide. Sulphide is oxidized biologically (favourably) in both aerobic and anoxic environments in which the activity of sulphide oxidizing bacteria is improved (Zhang et al., 2008). It has been reported that in the presence of nitrate as the electron acceptor, sulphide is firstly oxidized to S^0 and then to SO_4^{2-} . This phenomenon can be explained by the activity of nitrate-reducing sulphide-oxidizing bacteria which are only able to oxidize sulphide in the presence of nitrate (Zhang et al., 2008). According to the cited literature, biological sulphide oxidation in presence of nitrate could result in 65–95% sulphide removal (Okabe et al., 2003; Garcia de Lomas et al., 2006). Yang et al. (2005) showed that under anoxic conditions, nitrate is not capable of oxidizing sulphide chemically in sewer networks. Precipitation of dissolved sulphide in wastewater could be achieved through the addition of iron salts (ferric or ferrous chloride) (Firer et al., 2008) as well as precipitation with metals present in sewers including zinc, copper, nickel and manganese (Zhang et al., 2008).

Even though there are extensive studies highlighting the sewer processes involved in the dissipation of total dissolved sulphide, it is still uncertain which one is indeed the most dominating process. However some researchers explicitly claimed that oxidation of hydrogen sulphide was actually the dominant process on the dissipation of total dissolved sulphide (United States Environmental Protection Agency, 1974; Pomeroy and Parkhurst, 1977). This claim was rejected by studies conducted by Lahav et al. (2004, 2006). Lahav et al.'s studies state that hydrogen sulphide emission is actually the most contributing factor to the dissipation of total dissolved sulphide. The effective dissipation of total dissolved sulphide in wastewater can be achieved by dosing the problematic sewers with chemicals to manipulate the sewer conditions. The manipulation can be intended to inhibit the production of total dissolved sulphide or to eliminate the generation of hydrogen sulphide (H_2S) species so that it will not be released as hydrogen sulphide gas. A recent survey identified that there are five chemicals that are used by the Australian water industry to control the hydrogen sulphide gas generation (Ganigue et al., 2011): (i) *Oxygen*, which promotes aerobic condition in wastewater (ii) *Nitrates*, which promote anoxic condition in wastewater (iii) *Iron Salts*, which precipitate dissolved S^{2-} in the wastewater to harmless

iron sulphide (FeS) (iv) *Magnesium Hydroxide*, which slowly increases the pH of the wastewater up to a maximum value of 9.0 at which no hydrogen sulphide gas is released and (v) *Sodium Hydroxide*, which induces a “shock dosing” to wastewater to produce a pH of 13.0 at which no hydrogen sulphide gas is released.

This paper aims to derive a dissipation rate constant for total dissolved sulphide in a synthetic wastewater. This constant will be used to investigate the effect of different chemicals, being dosed to an experimental sewer pipe, on H_2S odour mitigation. The dissipation kinetics of total dissolved sulphide is not only influenced by the type of chemicals, but also affected by the hydraulic properties of the sewer network. Even though extensive studies have been carried out on the sulphide mitigation strategies through chemical dosing, most of them discuss the dissipation effect based on the concentration of chemicals applied and ignore the role of hydraulic properties of the wastewater flow in the dissipation process (de Haas, 2008; Ganigue et al., 2011, 2012; Nielsen et al., 2005). Therefore this study presents a thorough investigation on total dissolved sulphide dissipation under the influence of chemical dosing at different hydraulic conditions. Velocity gradient is selected as the parameter to represent the hydraulic conditions of the flow since it contains a complete combination of parameters representing the hydraulic characteristics such as velocity, depth and the density of wastewater.

Materials and methods

In order to investigate the effect of hydraulic conditions on the dissipation of total sulphide, two types of experiments were conducted in this study: (i) *Jar tests* to monitor the influence of mixing on the total dissolved sulphide dissipation (ii) *Experimental sewer tests* to mimic the real sewer system to which mitigating chemicals are dosed. The experimental sewer results were compared with the jar test measurements to evaluate the difference in mixing between the two types of experiments. Computed dissipation rate constant was then used to estimate the formation of hydrogen sulphide gas in sewer experiments.

Experimental sewer

An 18 m long poly vinyl chloride (PVC) sewer pipe with an internal diameter of 0.15 m, was used to conduct experiments (schematic and the actual experimental rig of the sewer system is given in Fig. 1). The pipe consisted of 3-m long sections joined by rubber seals. In order to monitor the effect of hydraulics in terms of varying slopes (1, 1.5 and 2%), the pipe was placed on a rig with an adjustable incline. Besides, 5 ventilation windows were cut in the pipe to enable adequate circulation of the gaseous phase, resulted in 6% of the total pipe length being fully open to the atmosphere. Other parts of the system include two centrifugal pumps that were utilized for circulating the simulated sewage solution as well as 2 high density polyethylene (HDPE) water tanks, the downstream one with an operational volume of 1 m^3 and the upstream one with an operational volume of 0.2 m^3 . The total water in the tank was kept at 0.4 m^3 throughout the experiments and both tanks were sealed at the top at the beginning of each experimental run.

Design of experiments

In order to monitor the effectiveness of mixing, the experimental sewer was run with synthetic wastewater that was prepared using fresh tap water. To establish an initial sulphide concentration, 25 g of fresh technical grade non-hydrated sodium sulphide (Na_2S ; Merck) was added to the downstream tank which contained 0.4 m^3 fresh tap water to make a concentration of $25.67 \text{ mg S L}^{-1}$ in the whole system. The artificial sewer was then

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