Chemical dosing for sulfide control in Australia: An industry survey

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ABSTRACT

Controlling sulfide (H_2S) production and emission in sewer systems is critical due to the corrosion and malodour problems that sulfide causes. Chemical dosing is one of the most commonly used measures to mitigate these problems. Many chemicals have been reported to be effective for sulfide control, but the extent of success varies between chemicals and is also dependent on how they are applied. This industry survey aims to summarise the current practice in Australia with the view to assist the water industry to further improve their practices and to identify new research questions. Results showed that dosing is mainly undertaken in pressure mains. Magnesium hydroxide, sodium hydroxide and nitrate are the most commonly used chemicals for sewers with low flows. In comparison, iron salts are preferentially used for sulfide control in large systems. The use of oxygen injection has declined dramatically in the past few years. Chemical dosing is mainly conducted at wet wells and pumping stations, except for oxygen, which is injected into the pipe. The dosing rates are normally linked to the control mechanisms of the chemicals and the dosing locations, with constant or profiled dosing rates usually applied. Finally, key opportunities for improvement are the use of mathematical models for the selection of chemicals and dosing locations, on-line dynamic control of the dosing rates and the development of more cost-effective chemicals for sulfide control.

1. Introduction

The production of sulfide is a critical problem in sewer systems due to the corrosion of sewer infrastructure and the generation of malodours (Boon, 1995; Pomeroy, 1959). Sulfide also has a detrimental effect on human health (USEPA, 1974). One of the main approaches adopted to date to mitigate such issues has been the dosage of chemicals to the wastewater (Melbourne, 1989). Among them, the addition of air or oxygen to prevent anaerobic conditions and to oxidise sulfide to sulfate (SO_4^{2-}) has

been widely used (Hvitved-Jacobsen, 2002; USEPA, 1992). Nitrate, another thermodynamically favourable electron acceptor, has also been employed over the last 70 years to prevent anaerobic conditions and thus to control odours and sulfide concentration in many environments (Bentzen et al., 1995; Bertrán de Lis et al., 2007). However, Mohanakrishnan et al. (2009) and Jiang et al. (2009) recently demonstrated that the actual mechanism leading to sulfide mitigation is the oxidation of H_2S to SO_4^{2-} via elemental sulfur by nitrate reducing-sulfide oxidising bacteria (NR-SOB). Strong oxidants

such as H_2O_2, NaOCl or $KMnO_4$ have also been applied for chemical sulfide oxidation (Tomar and Abdullah, 1994; USEPA, 1992). Another widely used strategy for H_2S mitigation is the addition of iron salts including ferrous chloride, ferric chloride and in some cases ferrous sulfate (Jameel, 1989; Padival et al., 1995). Ferrous ions (Fe^{2+}) precipitate sulfide by forming highly insoluble metallic sulfide precipitates (WERF, 2007). On the other hand, Ferric ions (Fe^{3+}) oxidise sulfide to elemental sulfur while being reduced into Fe^{2+}, which precipitates with sulfide to form ferrous sulfide precipitants (Dohnalek and Fitzpatrick, 1983). pH elevation is another strategy to control H_2S. A pH increase to 8.5–9, typically achieved through the continuous addition of magnesium hydroxide, prevents sulfide release to the gas phase (WERF, 2007). A recent study showed that pH elevation to 8.5–9 diminishes sulfate reducing bacteria (SRB) activity by 30–50% (Gutierrez et al., 2009), further enhancing the controlling effect. On the other hand, pulse addition of sodium hydroxide to increase pH to 12.5–13 for a short time (20–30 min) has been shown to inactivate SRB in the slime layer for a period of a few days to 2 weeks, effectively suppressing sulfide production (USEPA, 1992; WERF, 2007). The wastewater pulse or slug with high pH has to be isolated at the wastewater treatment plant (WWTP) and fed slowly into the system if it is not diluted in the collection system (USEPA, 1992). Finally, the use of microbial inhibitors such as formaldehyde (Zhang et al., 2008) or nitrite (Jiang et al., 2010a, b; Mohanakrishnan et al., 2008) have also been proposed, successfully demonstrated at laboratory and field-scale systems and in the near future may represent a more cost-effective methods for sulfide mitigation.

While many different chemicals are being used in practice for sulfide control and widely reported in literature, the extent of their use and the way how they are applied are not well known. The present work aims to establish the state of the art of chemical dosing for sulfide control in Australia, to summarise the key experiences of industry partners, and to identify ways to improve the dosing practices. Due to its warm climate in general, sewer corrosion and odour problems are widespread in Australia and are of major importance, and consequently sulfide control is receiving strong attention, with tens of millions spent each year. Nevertheless, it is important to note that sewer corrosion and odours are widespread problems, and chemical dosing for sulfide control has been conducted in many other countries as well, including Austria (Bertrán de Lis et al., 2007; Matsché et al., 2005), EUA (USEPA, 1992), Germany (Barjenbruch, 2003), Spain (Delgado et al., 1999) and United Arab Emirates (Vollertsen et al., 2011), among others.

The article aims to answer four main questions: (i) what chemicals are being used or have been used in the recent past to mitigate hydrogen sulfide production in sewer systems; (ii) to what extent each chemical is being used in terms of number of sites and wastewater flows treated; (iii) where each chemical is added; and (iv) how the dosing is carried out and controlled. These dosing practices are discussed in the context of the current understanding of the mechanisms by which each chemical works and improvement opportunities are identified. Questions for future research are also raised.

2. Methodology

2.1. Industrial survey

2.1.1. Design of the survey
The survey sought to identify the different chemicals dosed by the industry for sulfide control and the extent of their uses in terms of the number of locations, and the flow treated. The main characteristics of the pipes (dimensions, flow, hydraulic retention time, dosing location) where various chemicals are/were dosed were also collected. Other aspects covered by the survey included the selection or control of the chemical dosing rate, which is critical for successful sulfide control performance and costs. The survey was composed of four parts. Parts 1 and 2 covered general information of the systems, and specially aimed to identify the different chemical products used or in use. Part 3 targeted specific details of past and on-going sites, such as complete information of the installation and the dosing system, available instrumentation and off-line monitoring, as well as operation performance. Finally, Part 4 of the survey sought to identify dosing sites under design or construction, and collect detailed information of the site characteristics and dosing system. For further details see Appendix A.1, where the survey form is provided.

2.1.2. Conduct of the survey
The survey was conducted with seven water utilities across Australia, which provide sewage services to 13 million people (60% of the total population of the country). Table 1 lists all

Water utility	State	Mean minimum temperature in winter (°C)	Mean maximum temperature in summer (°C)	Annual rainfall (mm)
Table 1 – Water utilities surveyed, location and main climate characteristics of the areas.				
Allconnex Water	Queensland	9.3	29.3	1443.6
Barwon Water		6.5	25.3	648.9
Melbourne Water	Victoria			
South East Water Limited				
Sydney Water	New South Wales	8.7	25.6	1211.9
United Water International	South Australia	7.9	28.5	546.7
South Australian Water				
Water Corporation	Western Australia	8.0	30.4	734.0

these utilities, together with their location and main climate features (obtained from the Australian Bureau of Meteorology, www.bom.gov.au).

After the collection and preliminary analysis of the data, supplementary information was obtained with direct enquiries to the representatives of the water utilities to clarify specific issues.

3. Results and discussion

3.1. Dosing sites

The first step of the survey was cataloguing the different field sites where chemical dosage has been or will be carried out. Results are shown in Fig. 1.

In June 2010, a total of 165 dosing sites were identified through the survey. From these, 38 sites were reported to be no longer operative (in some of these, dosing was not required anymore, while others had been decommissioned because the dosing system had been proven not to be suitable to control sulfide production/release). At the time of the survey, chemical dosing was on-going at 114 sites and a further 13 dosing sites were due to be started in the near future.

The vast majority of dosing systems were located in pressure mains (162 sites), with only three gravity sites having been dosed with chemicals. These results clearly show a preference for control in rising mains where sulfide is normally generated in relatively large quantities, thus preventing possible adverse effects of H_2S at the discharge point or in the gravity section.

Sulfide production in a sewer pipe highly depends on factors like pipe dimensions (length and diameter), sewage flow and detention time. The characteristics of the surveyed pipes are presented in Fig. 2.

As can be observed in Fig. 2A, around 80% of the surveyed sites had pipe diameters between 0.15 and 0.5 m, while only 6% of the sites had a large pipe diameter (>0.5 m). 15% of the sites corresponded to very small pipes, with diameters below 0.15 m. The area to volume ratio (A/V) of a pipe is inversely proportional to the diameter of the pipe (A/V = 4/D, where D is the pipe diameter). Higher A/V values (i.e. smaller diameter

pipes) generally present a more significant biofilm contribution because sulfide production occurs mainly in biofilms attached to sewer walls (WERF, 2007). In addition, pipe diameter also has an impact on sewage hydraulic retention time (HRT).

With regards to the pipe length (Fig. 2B), almost half of the sites (44%) had a length below 1 km. Pipes between 1 and 5 km were 37% of the total, whereas longer pipes represented only around 20% (5–10 km, 16%; >10 km, 3%). Similarly to pipe diameter, pipe length also impacts on HRT. The larger the diameter and the longer the pipe, the larger the HRT will be for a given flow.

According to the average dry weather flow (ADWF) results presented in Fig. 2C, the majority of the dosing sites were located in pipes with very low flows (<0.5 ML d^{-1}, 34%). About 20% and 26% of the pipes had an ADWF between 0.5–1 ML d^{-1} and 1–5 ML d^{-1}, respectively, whereas only 20% of the pipes had a large flow (>5 ML d^{-1}).

With regards to the HRT (Fig. 2D), about 70% of the pipes with chemical dosing had an average HRT lower than 6 h. From the remaining systems, 19% have retention times in the range of 6–12 h, and only 12% of the pipes had HRT longer than 12 h. Theoretically, the longer the HRT of the sewage, the higher the sulfide production at the end of the pipe (Boon, 1995; Delgado et al., 1999; Sharma et al., 2008a, b). However, other parameters such as the A/V ratio (linked to the pipe diameter) and the wastewater characteristics also have an impact on sulfide production.

3.2. Chemicals applied

Seven chemicals are in use or were used in the recent past. Fig. 3 presents the number of sites that each of the chemicals are/were applied.

The most used chemical to mitigate the effects of sulfide, by number of sites, is presently magnesium hydroxide, which is applied at 30 locations. The second chemical in the ranking is sodium hydroxide, used for caustic shock to suppress activity of sulfate reducing bacteria (SRB) due to high pH. It is important to point out that sodium hydroxide is dosed all year round at only 16 of these 27 sites, while at the rest of the sites, sodium hydroxide is dosed during spring and summer
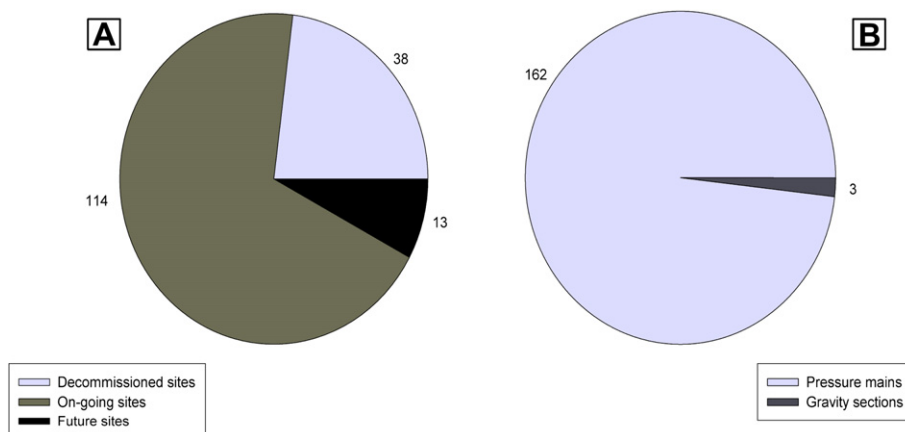

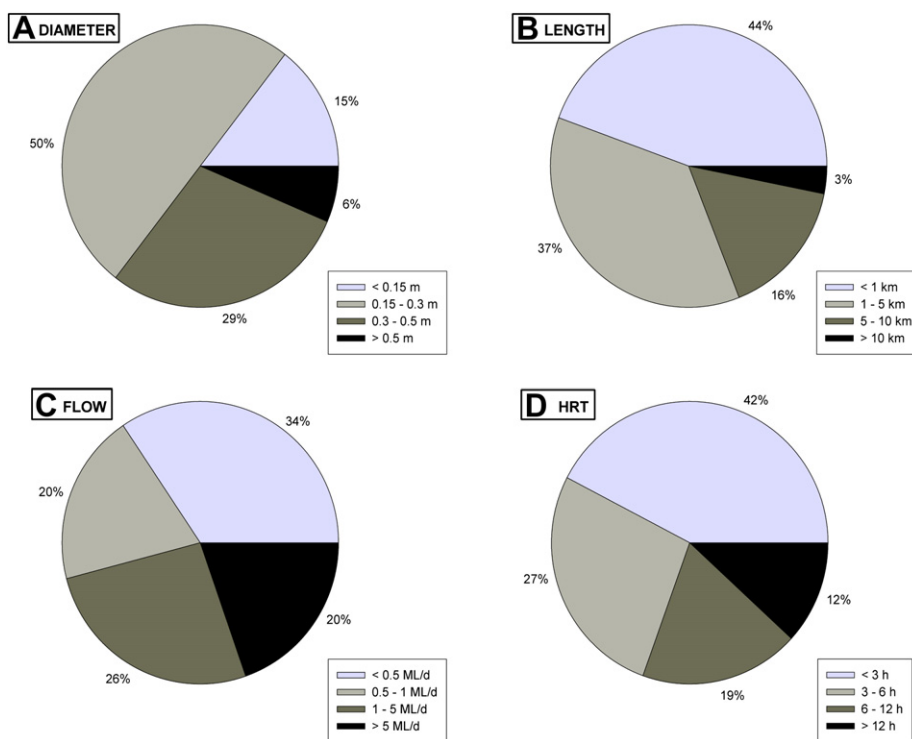Fig. 1 – (A) Status of identified sites; (B) types of pipes.

Fig. 2 – Main characteristics of the systems surveyed. (A) Pipe diameter; (B) pipe length; (C) average dry weather flow (ADWF); (D) hydraulic retention time (HRT).

seasons only. Nitrate and iron salts are used to a similar extent (25 and 22 sites, respectively). These two chemicals are also commonly used in Europe (Barjenbruch, 2003; Bertrán de Lis et al., 2007; Matsché et al., 2005). Oxygen was widely applied in the past to prevent anaerobic conditions, but its utilisation has significantly decreased due to its poor performance in some systems (27 decommissioned sites) and is now used in only 21 locations. Odour neutralizers are currently dosed at three sites, while biomaterials had been used in the past but were reported to be no longer applied at any site. As a final remark, a large number of biomaterials and bio-products are currently available in the market. However, the survey has shown that they are not gaining wide application in Australia. The effectiveness of several such products was tested recently in the laboratory of the Advanced Water Management Centre

at The University of Queensland. All the chemicals tested so far did not show any positive results (Gutierrez et al., 2010).

The number of application sites may not represent a full picture of the extent of usage of each product, and sewage flows receiving chemical dosing should be included in the analysis. Therefore the use of each chemical was also quantified based on the total flow treated for H_2S mitigation (calculated from the individual average flows). Only on-going and future sites have been considered in this analysis. Results are presented in Fig. 4.

Fig. 4 clearly illustrates the lower contribution of some of the most commonly used chemicals (in terms of number of sites). Only about 10% of the sewage was treated by sites with sodium hydroxide or magnesium hydroxide dosing (4.3 and 5.7%, respectively), while low percentages were also observed
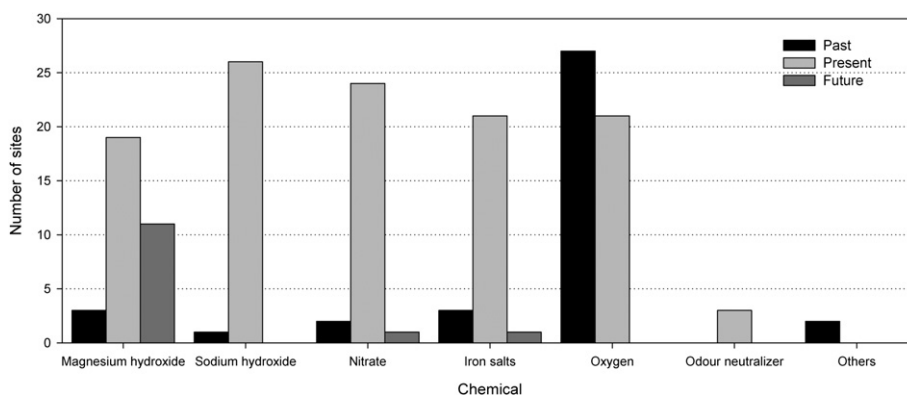

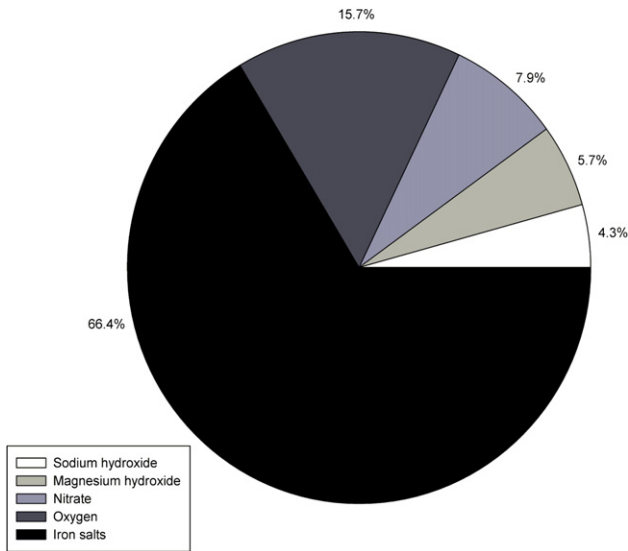**Fig. 3 – Chemical products used for sulfide control.**

Fig. 4 − Contribution of each chemical to the overall sulfide control.

for nitrate (7.9%). Although iron salts and oxygen are dosed at only a fewer sites, these two chemicals have a much higher contribution than the others in terms of sewage flow treated. Around 16% of the total sewage is treated with oxygen, while the sewage receiving iron salts dosing accounts for about 66% of the total sewage with chemical dosing.

Fig. 5 presents the analysis of the results based on the average ADWF (A) and pipe diameters (B) for the five most used chemicals: NaOH, $Mg(OH)_2$, NO_3^-, Fe^{2+}/Fe^{3+} and O_2.

It can be seen that sodium hydroxide is only used in systems with low flows (ADWF lower than 0.5 ML d^{-1}) and

small pipe diameters (more than 95% of the dosing is conducted in pipes with diameters smaller than 0.3 m). The mechanism for the caustic shock relies on the suppression of SRB from the biofilm attached to the sewer walls. In this respect, pipes with high surface area to volume ratios (A/V) are more favourable for this treatment since less amount of NaOH is required per volume of sewage. Therefore sodium hydroxide represents a cost-effective solution for sulfide control in small systems with low flow rates and high A/V ratios.

Similarly to sodium hydroxide, magnesium hydroxide is mainly applied in sewers with low flows and small diameters. About 80% of the magnesium hydroxide dosed sites are applied in sewers with average dry weather flows below 1 ML d^{-1} and pipe diameters between 0.15 and 0.3 m (Fig. 5B). Magnesium hydroxide effectiveness does not depend on the pipe size, but relies only on the pH and volume of sewage to treat (Parsons et al., 2003) and therefore could be suitable for sulfide control in systems of all sizes.

Fig. 5A shows that iron salts are preferentially used in medium and large systems (around 80% of the sites with flows larger than 1 ML d^{-1}). Accordingly, these systems have big pipe diameters (Fig. 5B). Iron salts dosing is a simple and cost-effective method for H_2S control. Precipitation reactions occur in the bulk liquid phase and iron salts dosing in the past has been considered not to have any interaction with the biofilm. Thus, iron dosing is appropriate for both small and large systems. It has gained a wider application in large systems because probably other chemicals are less suitable for sulfide control in such pipes. It should be noted that recent laboratory studies have shown that iron salts do interfere with biofilm activities. Zhang et al. (2009) showed that the activity of sulfide reducing bacteria in biofilms receiving $FeCl_3$ dosage was lowered by approximately 50% in comparison to that not
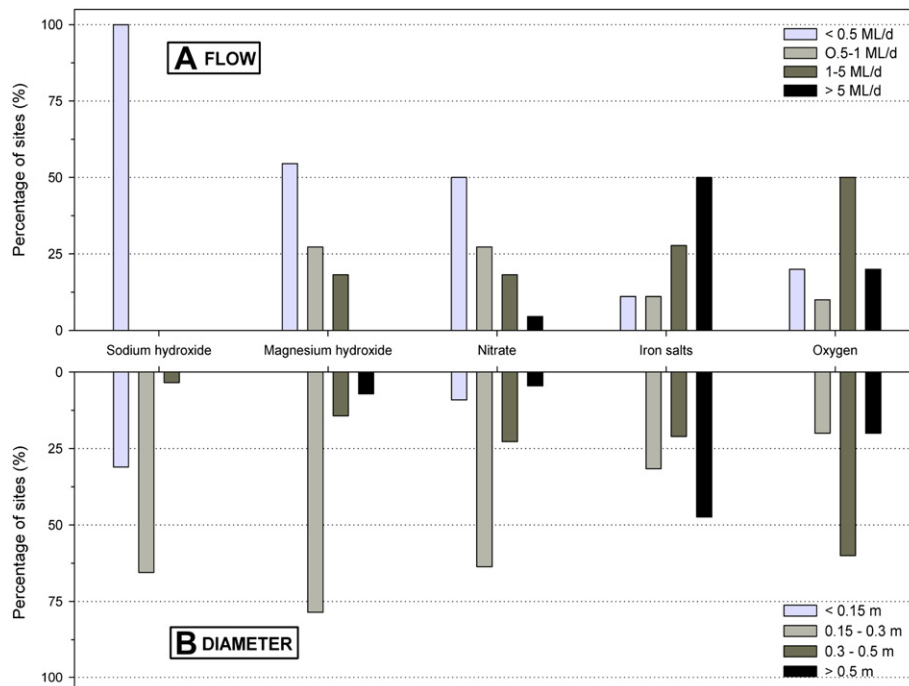

Fig. 5 − Site classification based on: (A) average daily flow rate of the sewer; (B) pipe diameter.

receiving FeCl$_3$ dosage. Zhang et al. (2010) further revealed that the interactions between iron salts and biofilm activity lowered the demand for FeCl$_2$ for sulfide control. Both of the above effects are positive, and may further enhance the prospect of the use of FeCl$_3$ or FeCl$_2$ for sulfide control in sewers.

Based on the results depicted in Fig. 5, oxygen is injected in systems of all sizes, but is mainly used in medium and high flow systems (pipes with ADWF between 1 and 5 ML d^{-1}) with large pipes (most of the pipes have diameters larger than 0.3 m). Oxygen relies on sulfide oxidation as the mechanism for H$_2$S control, although this can be chemical or biological (Gutierrez et al., 2008), i.e. this oxidation happens in both the biofilm and in the bulk liquid. Oxygen also promotes biological organic matter oxidation, with the subsequent consumption of oxygen and volatile fatty acids. Because this process primarily occurs in the biofilm (Sharma et al., 2011), oxygen is used more efficiently in pipes with large diameters (i.e. low A/V ratios) which usually deal with larger flows. Fig. 6 presents the theoretical O$_2$ utilisation efficiency for sulfide oxidation for different pipe diameters, assuming an oxygen consumption rate for biological sulfide oxidation of 5.6 gO$_2$/m^2 d (Gutierrez et al., 2008), an oxygen consumption rate for chemicals sulfide oxidation of 107 gO$_2$/m^2 d (Sharma and Yuan, 2010) and an oxygen consumption rate due to other heterotrophic microorganisms of 16 gO$_2$/m^2 d (Gutierrez et al., 2008). Oxygen consumption due to biological sulfide oxidation, chemical sulfide oxidation and heterotrophic consumption was calculated for different pipe diameters and expressed as a percentage of the total oxygen consumption.

Fig. 6 clearly shows that the larger the diameter, the higher the efficiency of oxygen utilisation for sulfide oxidation purposes. By analysing the contribution of each process, it can be seen that this is mostly due to the major role of chemical sulfide oxidation in the total sulfide oxidation, whereas the reduction of the A/V ratio for larger pipe diameters also implies the decline in the contribution of the biofilm processes (biological sulfide oxidation and also the heterotrophic consumption of O$_2$ for purposes other than sulfide oxidation).
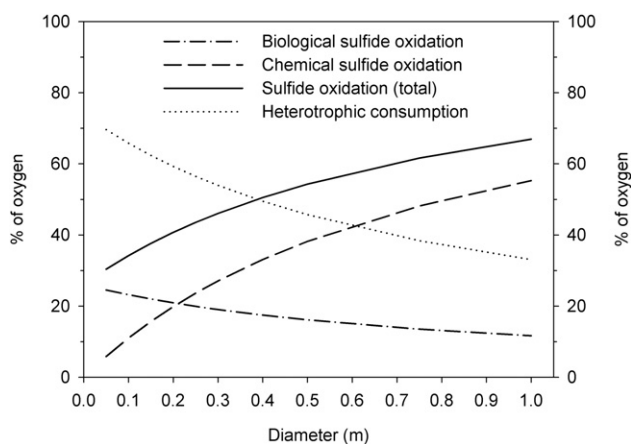

Fig. 6 – **Oxygen utilisation efficiency as a function of the pipe diameter for: biological sulfide oxidation, chemical sulfide oxidation, sulfide oxidation (total) and heterotrophic consumption.**

With regards to nitrate, it is also preferentially used in small systems, with only around 25% of the sites located in pipes with ADWF higher than 1 ML d^{-1} (Fig. 5A). Concerning the pipe dimensions, more than 60% of the sites where nitrate is dosed have a diameter between 0.15 and 0.3 m. Nitrate is an expensive chemical (de Haas et al., 2008), usually dosed as NaNO$_3$ or Ca(NO$_3$)$_2$ (Zhang et al., 2008). It does not inhibit SRB activity in the short- or long-term, and does not decrease the abundance of SRB in the sewer biofilm. Instead, nitrate addition to the start of rising mains increase SRB activity in downstream biofilms (Mohanakrishnan et al., 2009). Sulfide can be oxidised biologically by nitrate reducing-sulfide oxidising bacteria (NR-SOB), but chemical sulfide oxidation is almost negligible (unpublished results from the authors' group). Similar to oxygen, nitrate is also used as an electron acceptor by other heterotrophic bacteria, with subsequent nitrate consumption. Both the biological processes described above occur mainly in the biofilm (Mohanakrishnan et al., 2009). Hence, the effectiveness of nitrate does not rely on the A/V ratio. Therefore, nitrate addition is suitable for both small and large pipes, unlike oxygen, which is more suitable for large systems, However, the use of nitrate in large systems may be cost prohibitive due to its high price (Sharma et al., 2011).

As stated before, sewage HRT has a significant impact on sulfide production (Sharma et al., 2008b). HRT in systems with chemical dosing was also assessed to complete the analysis and identify if any of the five main chemicals is preferentially used to deal with certain conditions. Results are shown in Fig. 7.

It can be observed from Fig. 7 that the distribution of the HRT for four of the five chemicals, namely magnesium hydroxide, nitrate, iron salts and oxygen, was similar, indicating that these were not preferentially used for certain retention times or sulfide levels. Only sodium hydroxide is the exception to this. Sodium hydroxide is dosed to pipes with average HRT between 3 and 12 h. This may be due to the specific characteristics of these systems; small size pipes with low flows, as depicted in Fig. 5.

3.3.   Dosing location

The location where a chemical is dosed may determine the effectiveness of treatment and the operational cost. The survey showed that chemicals are dosed at the wet wells, pumping stations, an intermediate location along the rising main or at the discharge point of a rising main. These results are depicted in Fig. 8, where only current and future sites are considered.

In general terms, the preferred dosing location for the majority of the chemicals is before the wastewater enters the rising main (either at the wet well or the pumping station).

Sodium hydroxide was in all cases added at the wet well. This is in agreement with the theory that it should be dosed upstream of the rising main to effectively inhibit/kill all the SRB attached to the walls of the pipe.

Dosing of magnesium hydroxide is conducted primarily (60%) at either wet wells or the pumping stations. However, this chemical is also dosed, albeit to a less extent, directly into the main. It was even applied in one site at the discharge point of the rising main. Magnesium hydroxide is used to increase
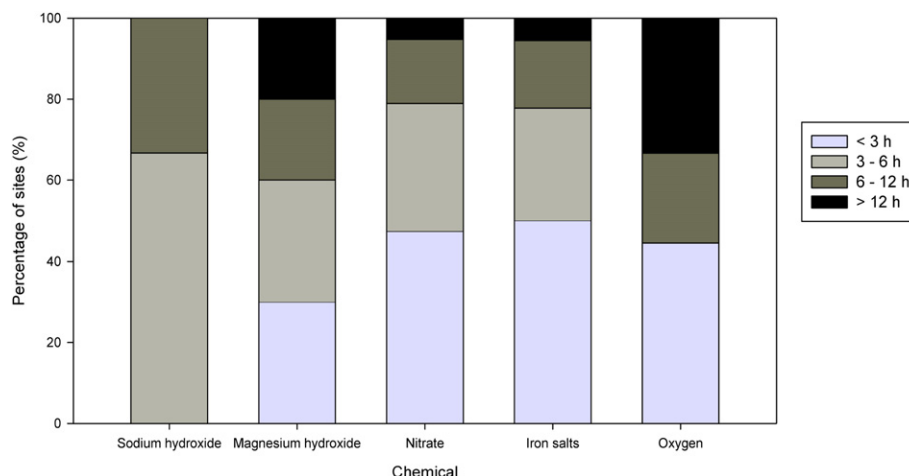
Fig. 7 — Site classification based on HRT for the different chemicals.

the pH to prevent sulfide transfer to the gas phase at rising main discharging points and in gravity sections. Therefore, the dosing location should not have a critical impact on the control of H_2S transfer. However, a recent study showed that high pH (pH > 8.5) can partially inhibit SRB activity, diminishing sulfide production (Gutierrez et al., 2009). As such, adding this chemical upstream would reduce its consumption to achieve the same level of control of sulfide transfer (Gutierrez et al., 2009). In this respect, the dosing of magnesium hydroxide upstream should be beneficial.

Around 70% of iron dosing was conducted at upstream locations (mainly at the wet well). The dosing location of iron salts is not important in terms of effectiveness of the chemical, as long as the hydraulic retention time (HRT) in the pipe after dosing allows sufficient time for sulfide precipitation (in the order of seconds according to Wei and Osseo-Asare (1995)). However, a recent lab-scale study demonstrated that the addition of Fe^{3+} significantly inhibits the SRB activity of anaerobic sewer biofilms (Zhang et al., 2009), although the same phenomenon is yet to be observed in real sewers. If this inhibitory effect is verified in real sewers, iron salts should preferably be added at upstream locations. A further benefit of

upstream dosage of iron salts is that sulfide would be controlled along the entire pipe. While iron salts may initially react with some other anions (e.g. phosphate and hydroxide) in the absence of sulfide, iron ions will be made available for sulfide precipitation when the latter is produced due to the lower solubility of FeS in comparison to iron phosphate and iron hydroxide precipitates (Zhang et al., 2009).

The survey also showed that nitrate is normally added upstream (95% of the dosing was conducted at the wet well or the pumping station), whereas oxygen was dosed at 90% of the sites along the rising main. Neither oxygen nor nitrate inhibit SRB activity in the short- or long-term, but their actual mechanism for H_2S control relies on sulfide oxidation (either chemical or biological) (Gutierrez et al., 2008; Mohanakrishnan et al., 2009). If oxygen was supplied at the beginning of the pipe, complete control of sulfide at the discharging points would require the entirety of the pipe to be oxic, which is not possible with the existing method of dosing (i.e. into wastewater when the pump is running) (Gutierrez et al., 2008). On the other hand, dosing nitrate upstream at a very high rate may ensure anoxic conditions along the whole pipe, although at a very high cost (Mohanakrishnan et al., 2009). In this
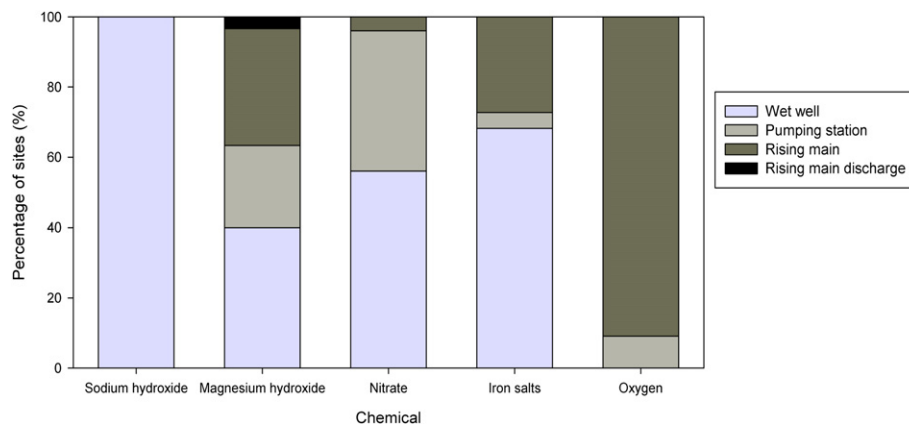

Fig. 8 — Dosing location of the chemicals.

respect, locating dosing points for oxygen or nitrate downstream (close to the end of the sewer or target point for sulfide control, but allowing adequate wastewater retention time downstream of dosing for complete oxidation of sulfide) is a more optimal solution in terms of performance and costs (Gutierrez et al., 2008; Mohanakrishnan et al., 2009).

3.4. Dosing rate control

Chemicals are dosed continuously or just during pumping events or periodically for several days/weeks. This mainly depends on the characteristics of the chemical and the dosing location. The dosing rate also has a critical impact on the effectiveness of sulfide mitigation and chemical consumption. According to the survey, four different dosing strategies are used by the industry: (i) intermittent dosing, where the same amount of product is dosed periodically; (ii) constant dosing, where the chemical is dosed at the same rate independent of the flow and wastewater characteristics; (iii) flow-paced dosing, where the amount of chemical delivered is proportional to the wastewater flow, and (iv) profiled dosing, where the dosing rate is variable according to a pre-defined profile. The reported dosing strategies used by industry are shown in Fig. 9.

As can be observed in Fig. 9, sodium hydroxide is only added intermittently and for a short period (one to five pumping cycles) to reach pH 10–11 (O'Gorman et al., 2011). This is because of its unique mechanism – SRB activity suppression by caustic shock. Magnesium hydroxide, nitrate and oxygen sites are mostly operated at pre-defined dosing rates. Around 50% of the iron dosing sites used pre-defined profile dosing rates, while the other half used constant rates. Constant rates were also used at about 30% of the nitrate and oxygen dosing stations. Finally, flow-paced dosing was seldom applied and was only of relative importance for sites with magnesium hydroxide dosing (25–30%). This is reasonable, given the fact that magnesium hydroxide dosing relies mainly on the volume of sewage and not on the sulfide concentration.

Finally, Table 2 summarise the current industry practice in terms of dosing rates and costs for the different chemicals. The effectiveness related to these dosing rates is however not known.

As can be clearly observed, dosing levels differ from one chemical to another and present a wide range. This is due to the different characteristics of the systems where chemical dosing is conducted. Taking into account the dosing frequency and flow, sodium hydroxide dosing rates from 11 to 28.6 L of NaOH (50% w/w) per ML of sewage were reported in the survey. This chemical relies on the suppression of SRB from the pipe biofilm due to the caustic shock. Hence, the pipe diameter plays a critical role and dosing requirements dramatically increase with pipe diameter. Magnesium hydroxide dosing levels ranged from 48 to 157 kg $Mg(OH)_2$/ML of sewage. The effectiveness of this chemical is independent of the sulfide levels or the pipe diameter, depending mainly on the buffer capacity of the sewage. In addition, biological acidifying reactions could take place along the pipe so longer pipes may require additional $Mg(OH)_2$ dosing. Nitrate, oxygen and iron salts present also a wide dosing rate range. Nitrate and oxygen oxidise sulfide, while the principle behind iron salts is the sulfide precipitation. In this respect, the dosing of all three chemicals is critically governed by sulfide levels in the pipe. Other aspects such as the dosing location or the pipe length and diameter may also partly explain the disparity among the results.

When the costs are analysed, nitrate dosing is found to be the most expensive option, with a maximum cost of up to $483.6/ML. Similar chemical costs were reported for Magnesium hydroxide (48.7–159.3 $/ML) and iron salts dosing (10.9–170.6 $/ML). Chemical costs for iron salts dosing were comparable to those reported by Matsché et al. (2005) for sulfide control in Austria (42–77 $/ML). The dosing costs for intermittent NaOH dosing were slightly lower, 39.6–99.1 $/ML, although the constraints of this technology have to be taken into consideration. Finally, these figures show oxygen to be the least expensive chemical with a maximum dosing cost of 74 $/ML of sewage.

3.5. Chemical dosing performance

Assessing the performance of chemical dosing was one of the objectives of the survey (see Appendix A.1, sections 3.C and 4.C). However, results showed that systems with chemical dosing were seldom monitored and little data was available. For most of the sites, neither on-line nor periodical
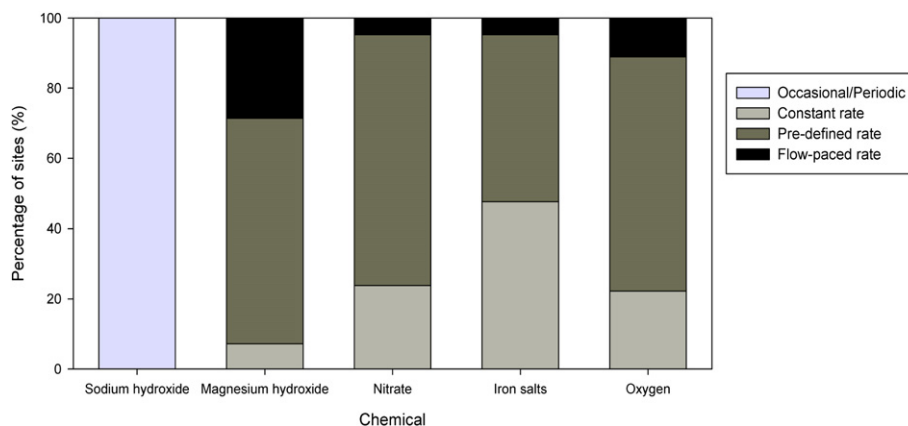

Fig. 9 – Dosing rate control of chemicals.

Table 2 – Chemical dosing current industry practice.		
Chemical	Dosing levels	Chemical cost[b]
Sodium hydroxide[a]	11.4–28.6 L NaOH/ML[a]	39.6–99.1 $/ML[a]
Magnesium hydroxide	47.9–156.6 kg $Mg(OH)_2$/ML	48.7–159.3 $/ML
Nitrate	1.33–15.5 kg $N\text{-}NO_3^-$/ML	41.3–483.6 $/ML
Iron salts	3–47 kg Fe/ML[c]	10.9–170.6 $/ML
Oxygen	15.8–91.5 kg O_2/ML	12.8–74.0 $/ML

a To reach pH 10–11 using NaOH 50% w/w.
b Based on the following chemical prices in Australian dollars: $69.3/20L NaOH (50% w/w); $590/tonne $Mg(OH)_2$ 58% w/w; $1010/m^3$ $Ca(NO3)_2$ 50% w/w; $526/tonne $FeCl_3$ 42% w/w; $1.15/m^3$ O_2 99.5% w/w.
c Dosing levels of up to 705 kg Fe/ML were reported, but were excluded from this comparison as non-representative (abnormally high).

monitoring of dissolved sulfide or gas phase H_2S was conducted. Lack of odour complaints were, in most of the cases, used as an indication of the effectiveness.

4. Opportunities for operational improvement and future research

Based on the results of the survey, several opportunities for improvement as well as future research questions have been identified.

4.1. Model-based support for the selection of chemicals, dosing locations and dosing rates

The current selection of chemicals and the design of its dosing locations and rates are mainly based on experience (i.e. iron salts are more suitable for large systems, or oxygen has to be dosed directly into the pipe). However, there are many factors to be considered. The selection and design should be made based on specific features of each site and characteristics of the sewage. In recent years, powerful mathematical models such as the SeweX model (Sharma et al., 2008b) and the WATS model (Hvitved-Jacobsen et al., 1998) have been developed to support the decision making and have indeed been demonstrated in several cases (de Haas et al., 2008; Sharma et al., 2008a). However, these models are yet to be taken up widely.

4.2. On-line control of the dosing rate

Currently constant, flow-paced and profiled dosing rates are used to control chemical dosing. These are commonly based on empirical guidelines developed, again, through experience. However, sulfide concentration and flows have a dynamic behaviour over a day, and constant or flow-paced dosage could lead to over dosage during periods with low levels of sulfide production, and under dosage during some other periods. In some cases, profiled dosing with variable dosing rates is applied based upon historical data (flow rate, sulfide concentration, etc.). However, this strategy may not be

effective as the dynamics of each sewer system is different, and even for the same sewer system the conditions vary from day to day (Sharma and Yuan, 2009). Recent development in on-line sensor technology has made the on-line measurement of dissolved sulfide levels possible (Sutherland-Stacey et al., 2008). In this respect, dynamic dosing of chemicals based upon on-line measurement of parameters such as flow rate and liquid phase sulfide concentration may achieve better sulfide control with lower chemical costs. However, the current high price of the dissolved sulfide sensors makes on-line control economically non-viable for small systems. Future work should address this issue by developing more affordable and reliable sensors for dissolved sulfide measurement. In addition, due to the different mechanisms of the chemicals, specific control algorithms need to be developedfor each chemical to ensure optimised dynamic control.

4.3. More cost-effective chemicals

All the above-mentioned chemicals (except for NaOH) require continuous dosing of the product, which results in high chemical supply costs. In this respect, research is needed to develop more chemicals to directly target the activities of sewer biofilms. Some biomaterial products are available, but there has been little peer-reviewed evidence showing their effectiveness. However, recent lab studies reported the inhibitory effect of nitrite/free nitrous acid (FNA) on SRB and methanogenic activities in sewer biofilms (Jiang et al., 2010a, b, 2011). FNA as low as 0.18 mg-N/L can suppress sulfide production after 24-h of exposure. The suppression is followed by a slow recovery (several days to several weeks) after stopping the FNA addition (Jiang et al., 2011). FNA has appears to be promising chemical, but its dosage requires further optimisation.

5. Conclusions

An industrial survey was conducted among seven major Australian water utilities, cataloguing the different field sites where chemical dosage was/is/will be carried out. A total of 165 sites were identified, the vast majority of them being located in pressure mains.

Seven different chemicals were or are in use: Magnesium hydroxide, sodium hydroxide (caustic shock), nitrate, iron salts, oxygen, odour neutralizers and other biomaterials. Magnesium hydroxide is the chemical applied at most sulfide control sites (30), followed by sodium hydroxide (27) and nitrate (25). However, when taking into account the flow treated, the dosing of iron salts is used to control sulfide in approximately 66% of the sewage treated. Magnesium hydroxide, sodium hydroxide and nitrate are used mainly for small pipes with low flows and their total contribution is only around 18% of the total flow treated with chemicals for sulfide control.

Chemicals are normally dosed at wet wells or pumping stations, except for oxygen, which is mainly injected directly into rising mains. The dosing of nitrate in these upstream locations is likely to result in either low H_2S control efficiency

or high chemical costs, while the dosage of other chemicals at such locations appear appropriate.

Constant dosing and profiled dosing are the two methods predominantly used for dosing rate control. Flow-paced control is also in use. None of the 165 sites use or used on-line control of the dosing.

Finally, there are several key opportunities to achieve more effective and cost-effective sulfide control. Mathematical models are now available to support the selection of the most suitable chemical, dosing location and dosing control for each case. On-line control of dosing rate may also improve the effectiveness of the dosing and reduce chemical costs. Also, more cost-effective chemicals need to be developed, which does appear to be possible.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.watres.2011.09.054.

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