



## Simultaneous use of caustic and oxygen for efficient sulfide control in sewers



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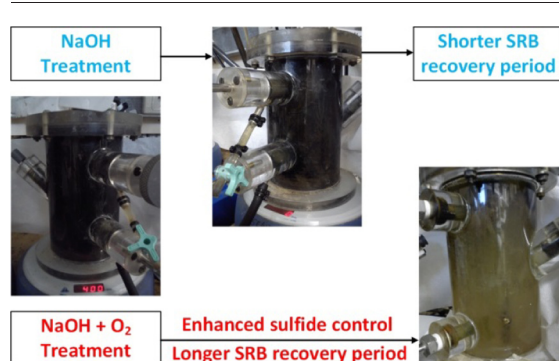
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### HIGHLIGHTS

- Long-term efficient sulfide control in lab-scale sewer by NaOH-O<sub>2</sub> combined dosing
- The addition of O<sub>2</sub> to caustic shock resulted in prolonged sulfide recovery period.
- Synergistic effect of NaOH and O<sub>2</sub> led to a reduction in CH<sub>4</sub> production by 99%
- Intermittent O<sub>2</sub> addition reduced the dosing frequency for NaOH by 50%.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 4 April 2017

Received in revised form 23 May 2017

Accepted 24 May 2017

Available online xxxx

Editor: D. Barcelo

#### Keywords:

Sewer corrosion  
Sulfate reducing bacteria  
Sulfide abatement  
Dynamic modelling  
Caustic shock-loading  
Oxygen

### ABSTRACT

Periodic caustic shock-loading is a commonly used method for sulfide control in sewers. Caustic shock-loading relies on the elevation of the sewage pH to  $\geq 10.5$  for several hours, thereby removing sewer pipe biofilms as well as deactivating SRB activity in the remaining biofilm. Although a widely used method, SRB activity is often not completely inhibited, and as such sulfide is still being generated. Here, we propose and experimentally demonstrate an innovative approach which combines caustic with oxygen, another commonly used method, as a dosing strategy for overcoming the drawbacks of caustic shock-loading. Six laboratory-scale rising main reactors were subjected to three dosing schemes over a period of three months, namely (i) simultaneous caustic and oxygen addition, (ii) caustic addition and (iii) no chemical addition. Our results showed that the combination of caustic and oxygen achieved efficient sulfide control, leading to a prolonged biofilm recovery period in between caustic shocks. In addition, methane emissions were reduced to a negligible level compared to caustic treatment only. To translate the findings to real-life application, the key parameters obtained during the long-term lab-scale experiments were subjected to extensive simulation studies using the SeweX model under a wide range of conditions commonly found in sewers. Overall, this study highlights the potential of periodic shock-loading and intermittent oxygen injection as combined dosing strategy for efficient sulfide control in sewers.

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## 1. Introduction

Hydrogen sulfide generation by sulfate reducing bacteria (SRB) in sewer pipes is a major issue in sewer management globally (Pikaar et al. 2014). The emission of hydrogen sulfide into the sewer atmosphere causes concrete corrosion as well as the release of obnoxious and toxic odours, posing a threat to sewer workers (Vollertsen et al. 2008). Current sulfide control strategies mainly involve chemical addition to either prevent hydrogen sulfide generation or mitigate its effects after its formation (Zhang et al. 2008). Two of the most commonly used chemicals are periodic caustic shock-loading and oxygen injection (Ganigue et al. 2011).

Periodic caustic shock-loading, by raising the pH of the sewage to >10.5 for a short period of time (i.e. 2–6 h), relies on the removal of the biofilm from the sewer pipes as well as deactivating SRB activity in the remaining biofilms responsible for hydrogen sulfide formation (Gutierrez et al. 2014; O’Gorman et al. 2011; WERF 2007). While considered a cost-effective method, the sewer pipe biofilm is not completely removed after a dosing event. As the SRB activity in the remaining biofilm is not completely inhibited, sulfide is still being generated (Gutierrez et al. 2014). In addition, the re-growth of SRB can already commence within 1 to 3 days after a dosing event and may achieve complete SRB recovery within 3 to 14 days, depending on local conditions and sewer pipe design (Gutierrez et al. 2014; WERF 2007).

In addition to deactivating SRB, it has been reported that pH elevation of sewage to above 8.6 deactivates methanogenic archaea (MA) (Gutierrez et al. 2009). Methane emissions from sewer systems to the atmosphere are also problematic as methane is a potent greenhouse gas that substantially contributes to the carbon footprint of water utilities (Guisasola et al. 2008a, Guisasola et al. 2009). Hence, inhibiting methane production in sewers is considered to be an additional benefit of using periodic caustic shock-loading as a sulfide control strategy.

Oxygen injection suppresses the biological activity of SRB by maintaining oxic conditions as well as oxidizing sulfide either by chemical or biological sulfide oxidation (Gutierrez et al. 2008; Nielsen et al. 2003). While considered as one of the cheapest sulfide control methods, a major limitation of oxygen injection is its poor performance in some systems due to inappropriate choices of dosing locations and/or dosing rates (Ganigue et al. 2011). The diffusion of oxygen into the sewer biofilm largely determines the effectiveness of suppressing the SRB activity (Gutierrez et al. 2008). Under normal sewer conditions, dissolved oxygen does not fully penetrate into the biofilm, and as such the generation of sulfide continues in the anaerobic inner part of the biofilm (Gutierrez et al. 2008). The same holds true for MA, as these grow in the deeper layers of the biofilm and oxygen can only partially inhibit their activity (Ganigué and Yuan 2014). Moreover, the growth of heterotrophic biofilm caused by aerobic conditions results in an increase in oxygen uptake rate. Consequently, aerobic conditions cannot be maintained throughout the entire sewer pipe with sulfide production still occurring (Gutierrez et al. 2008).

Although periodic caustic shock-loading and oxygen injection have been widely used as individual sulfide (and methane) control strategies, simultaneous use of these two chemicals has to our best knowledge never been investigated. It may however allow for more efficient sulfide (and methane) control. Periodic caustic shock-loading (partly) removes the sewer pipe biofilm during each dosing event (Gutierrez et al. 2014; O’Gorman et al. 2011; WERF 2007). This results in a thinner biofilm which would allow oxygen to penetrate further into the biofilm, thereby contacting the remaining SRB in the deeper layer of the biofilm. In this way, a better suppression of SRB may be achieved, leading to a prolonged biofilm recovery period in between caustic shocks.

Recently, the simultaneous electrochemical generation of caustic and oxygen from sewage for sulfide control was successfully demonstrated (Lin et al. 2015). Using a three-compartment electrochemical cell, sewage was continuously oxygenated in the anode compartment whereas the cathode was operated in batch mode thereby producing a

moderate strength caustic solution (Lin et al. 2015). It was hypothesized that in this way, caustic can be periodically applied to the sewer pipe to clean sewer biofilms while sewage is continuously oxygenated and as such could suppress the residual biofilms between caustic shocks (Lin et al. 2015). While the above-mentioned study highlighted the practical and economic feasibility of simultaneous production of caustic and oxygen for sulfide control in sewers, the potential synergistic effect of caustic and oxygen on sewer biofilm was not investigated.

In this study, we therefore investigate the potential synergistic effect of caustic and oxygen addition as combined dosing strategy for sulfide control in sewers. Using six laboratory-scale sewer rising main reactors, we conducted long-term experiments using three dosing schemes, namely (i) simultaneous caustic and oxygen addition, (ii) caustic addition and (iii) no chemical addition. Subsequently, to translate the result to real-life applications, the key parameters obtained were subjected to an extensive set of dynamic simulations using the SeweX model under a wide range of conditions commonly found in sewers.

## 2. Material and methods

### 2.1. Laboratory sewer reactors

Laboratory-scale rising main sewer reactors in three parallel lines were used, as depicted in Fig. 1. The three parallel lines were defined as the caustic and oxygen line (the first reactor RE1 and the second reactor RE2), the caustic line (the first reactor RE3 and the second reactor RE4) and the control line (the first reactor RC1 and the second reactor RC2). Each line comprised of two completely sealed reactors connected in series. The reactors were entirely shielded with aluminum foil to prevent the sewage and biofilms from light exposure. A continuously mixed 1 L schott bottle mimicking a wet-well was placed at the beginning of each line for the addition of caustic and oxygen and caustic, respectively. No chemical addition took place in the control line. A 20 L composite sample container was equipped at the end of each line for collecting 24-h composite effluent. The sewer reactors, each with a volume of 750 mL, an inner diameter of 8 cm and a height of 15 cm, were made of Perspex™ and designed to mimic anaerobic sewer rising mains, as described in detail by Gutierrez et al. (2011). Ten Plastic Kaldnes carriers with dimensions of 9 mm height and 7 mm diameter (Anox Kaldnes, Norway) were equipped on a stainless steel rod inside each reactor for analysis of the microbial composition. The biofilm surface area in each reactor was calculated at 0.05 m<sup>2</sup>, resulting the area to volume (A/V) ratio of 61.4 m<sup>2</sup>/m<sup>3</sup>. Each reactor lid was equipped with a 70 mL container filled with sewage to avoid any vacuum or entry of air during sewage displacement. All reactors were continuously stirred using magnetic stirrers (Heidolph MR 3000), creating turbulent conditions of 0.44 Pa shear stress, mimicking real sewer conditions as previously determined by Sun et al. (2015).

Fresh sewage was collected from a local pumping station in Brisbane on a weekly basis and immediately stored at 4 °C to minimize biological transformation of the sewage. All lines were exposed to 18 uneven pumping events daily (i.e. 3 repeated cycles with each cycle consists of 6 uneven pumping events) with a volume of 750 mL sewage fed to each line during each pumping event (see supplementary material, Fig. S1). Sewage was heated up to 24 ± 3 °C using a water bath before being fed to reactors. The typical domestic sewage contained 10 to 25 mg/L sulfate-S, <3 mg/L dissolved sulfide-S and negligible amount of sulfite and thiosulfate. Methane and dissolved oxygen (DO) concentrations were also negligible. The average pH of the sewage influent used in the experiment was 7.4 ± 0.4.

### 2.2. Operation conditions

The experiments were divided into two phases: the baseline and the experimental phase. During the baseline phase, the system was operated for 9 months without the addition of caustic and oxygen in order to

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