The Cloevis® Biofilm Removal System: Results from Early US Commercial Applications

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Abstract

Free Nitrous Acid (FNA) is the active agent underlying a new biofilm removal technology ("Cloevis") for controlling sulfide production in wastewater force mains. The technology was developed at the University of Queensland and, after initial field testing in Australia, commercial field tests in the U.S. began in late 2015. These early test sites were chosen to reflect a range of force-main situations, including: short vs long retention times; small vs large wastewater flows; and force mains heretofore treated with nitrate, iron salts, or no treatment. In all cases, the Cloevis technology was able to bring the sulfide levels under target limits, although auxiliary (complementary) treatments are needed in two scenarios: where pre-existing sulfide enters the force main segment either through the influent flow or through a manifolded (interconnecting) force main; and where the candidate force main has accumulated deposits of fats, oils, and grease that coat and protect the biofilm. This paper will describe the Cloevis technology and discuss the results from three of the early field tests in the U.S.

Keywords

Sulfide Control, Corrosion Control, Odor Control, Force Mains, Biofilm Treatment, FNA, Free Nitrous Acid, Cloevis

Introduction

Sulfide production within municipal wastewater collection systems poses significant challenges to engineers who manage risks associated with nuisance odors, infrastructure corrosion, worker safety, and treatment plant performance. Considerable resources – both capital and operating – are spent to minimize these risks. Like most problems, the best solutions address the root cause; however, unfortunately, this has not been the case for the collection system sulfide generation problem, largely due to the dearth of compelling sulfide control technologies.

Relevance of sulfide production within biofilms. A large majority (>90-95%) of the sulfide produced within wastewater collection systems occurs within the biofilm affixed to the walls of force main piping systems. Except for slow-moving interceptor flows, most gravity lines are net positive in D.O. and do not contribute to the sulfide loading. The source of the sulfide is Sulfate-Reducing Bacteria (SRB) that reside deep within the biofilm, and are 'protected' by layers of microbial communities that 'condition' the wastewater for the underlying SRBs.

[1] 'Cloevis' is a registered trademark of UniQuest, Pty Ltd – a business/technology incubator associated with the University of Queensland

(Intermittent) biofilm treatment versus (continuous-feed) liquid treatment. Most chemical agents used to control sulfide do not impact the SRBs but rather react (directly or indirectly) with the sulfide as it permeates through the biofilm and into the wastewater flow. Consequently, these agents must be dosed continuously. On the other hand, biofilm treatments impact the source of sulfide generation (the SRBs), which affords the possibility of intermittent treatments since time is needed for the SRBs to recover.

Relative to continuous-feed treatments, intermittent biofilm treatments have the advantages and disadvantages listed in Figure 1 (below).

Figure 1. Advantages / Disadvantages of intermittent biofilm treatments

Advantages:
- *Minimizes chemical use*
- *Savings increase with sulfide loadings*
- *Allows option of no onsite storage of chemicals*
- *Complementary to continuous treatments*

Disadvantages:
- *Addresses only sulfide generated within the treatment pipe segment*
- *Limited to smaller upstream flows (to avoid plant impacts)*
- *Can be labor/logistically complicated*

Current biofilm treatment techniques. Caustic shocking is the biofilm treatment technique currently used in the industry, and is characterized by adding sufficient NaOH (typically 10-20 g/L) to raise the wastewater pH to >pH 12 for a period of >30 minutes.[1] Experience at municipalities in Southern California has highlighted two negative aspects of caustic shocking:

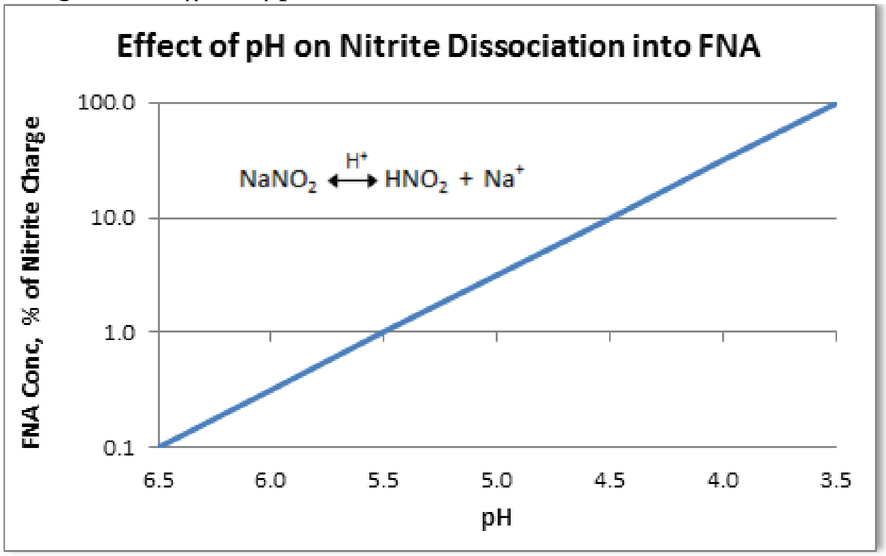
- Plant impact: Biotreatment interference through pH excursions and monovalent:divalent cation imbalances.
- Fast recovery: Complete suppression of sulfide production is short-lived, with typical summertime results being 20% recovery within 1-2 days and full recovery within 5-8 days.

Other biofilm treatments have been previously tested or are being used sparingly in the industry. These include metabolic modifiers (anthraquinone) and oxidizing agents (chlorine dioxide and peracetic acid). Oxidizing agents have the benefit of dissipating/decomposing quickly downstream of the FM discharge, thereby negating treatment plant risk. However, the applications cost in labor, equipment, chemicals have proven prohibitive.

Background

Free Nitrous Acid (HNO_2) is the protonated acid dissociation product of the nitrite ion, which (per Figure 2) begins at approximately pH 6.5 and is complete below pH 3.5.

Figure 2. Effect of pH on nitrite dissociation into FNA



$S_{N\text{-}NO2} / (K_a \times 10^{pH})$, where $K_a = e^{-2300/(273+T(deg\text{-}C))}$

The effect of FNA on wastewater microbiology has been reported by Zhao, et.al.[2] who found that nitrifying bacteria experience threshold inhibition at FNA concentrations as low as 0.01 mg-N/L. While the nitrite ion can impact microbiology at higher concentrations (and exhibits significant toxicity to aquatic organisms), the prevalence of nitrite-oxidizing bacteria in wastewater means that (like nitrate) denitrification proceeds rapidly once the pH returns to near neutrality.

The Cloevis technology was developed by researchers at the University of Queensland to target SRB growth within piping / conveyance systems, particularly municipal wastewater force mains.[3-5] These controlled laboratory tests showed:

- Nitrite dosing is a promising technology for controlling sulfide and methane formation in sewers, due to the known inhibitory/toxic effect on SRBs and methanogenic *Archaea spp*.
- The inhibition level was dependent on nitrite concentration, exposure time, and dosing interval. Model-based analysis showed the recovery was likely due to the regrowth of SRBs and methanogens.
- FNA doses as low as 0.26 mg-N/L were able to suppress sulfide production after 12 hours exposure, whereas a dose of 0.09 mg-N/L was able to suppress methane production after six hours exposure.
- The viable fraction of microorganisms within the sewer biofilm was found to decrease from about 80% prior to treatment to 5-15% after treatment.

More recently, the technology was proven in field tests conducted in Australia by the Queensland researchers.[6] These tests showed:

- Intermittent dosing of FNA can achieve effective control of sulfide production in rising main sewers. One single dose for 8-24 h can provide lasting effectiveness up to 10 days for an average reduction of sulfide by 80%.

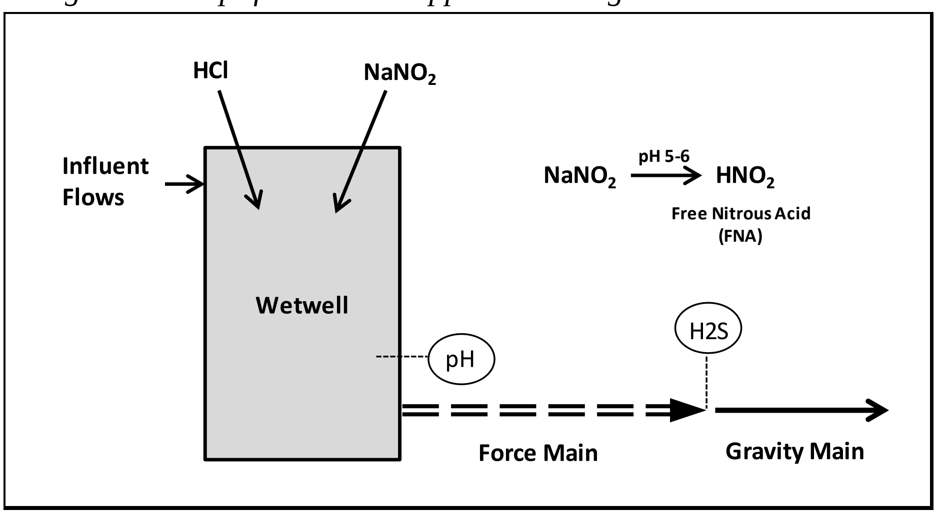
- No biofilm adaptation to FNA was observed through the 6-month trial. Instead, successive dosing may achieve better control efficiency due to repetitive weakening of the biofilms.

The Cloevis technology has since been licensed to USP Technologies, as the exclusive provider in North America. Within the past few months, several commercial field tests have been completed in Florida and California, three of which are described in this paper.

Methods and Procedures

The general prescriptive application of the Cloevis technology involves contacting the force main biofilm with wastewater containing approx. 0.2 mg/L NO_2-N FNA for a defined period, typically 6 - 24 hours. The FNA is created *in-situ* in the wetwell by adding sodium nitrite precursor and lowering the wastewater pH to dissociate a portion of the nitrite to FNA (Figure 3). Vapor H_2S levels at the FM discharge manhole were datalogged to measure performance, and grab samples were periodically taken at the FM discharge and analyzed for total/dissolved sulfide, pH and residual nitrite/nitrate.

Figure 3. Simplified Cloevis application diagram

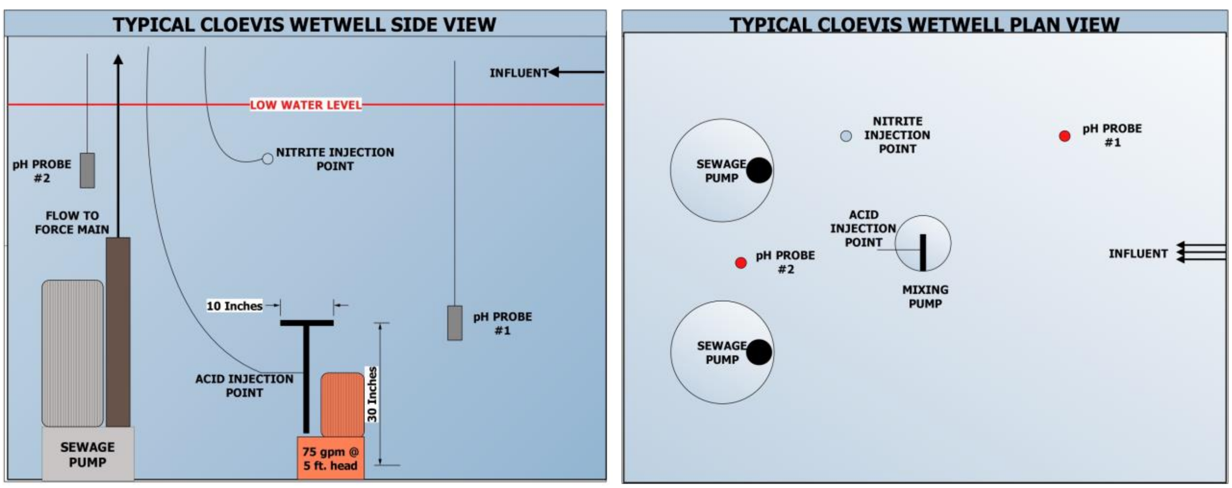


The equipment needed to apply the Cloevis technology consists of two subsystems supported by data acquisition and telemetry for remote operation. The first subsystem is the chemical storage and dosing module which, depending on sizing and site constraints, can be either stationary, temporary (for applying treatments), or completely mobile (contained). Figure 4 shows the temporary module used in the first case study.

Figure 4. Photo of a small Cloevis storage/dosing module (150,000 gpd wastewater flow).

The second subsystem is the chemical injection/mixing/controls (IMC) module which is placed in the wetwell to ensure accurate dosing and complete mixing (Figure 5). The module includes a submersible pump that draws in wastewater, mixes in the acid, and distributes the pH-adjusted water throughout the wetwell. Acid feed is controlled by two separate pH probes situated in different parts of the wetwell, and nitrite feed is paced to the influent wastewater flow.

Figure 5. Schematic of the chemical injection/mixing/controls (IMC) module



Implementation of the Cloevis technology for new sites proceeds through two phases. The first phase is the initial biofilm cleaning phase where 2-3 Cloevis treatments are repeated over a 3-5 day period. This has the effect of sequentially removing layers of biofilm to expose the underlying SRBs, and is observed as sequential step-changes in H_2S removal until complete suppression is observed. After a few days, this is followed by a slow prolonged recovery of H_2S production (over 2-3 weeks). Once the initial cleaning is complete, the second phase of routine periodic maintenance treatments can begin.

Results

<u>Case Study 1</u>

Force main length .... 1246 feet
Force main diameter .... 8 inches
Force main retention time ...... 2 hours
Wastewater flow .... 0.025 MGD

The first case study is a small, straightforward intermittent pumping line (i.e., no influent or extraneous sulfide inputs) that had received no prior sulfide control treatment. Baseline vapor H_2S readings over a two-day period at the force main discharge are shown in Figure 6. The profile shows retention times through the midnight hours increase to six hours or more, which results in repetitive H_2S excursions with each pump cycle until the stagnant flows are purged through the system. Hence, the average of 15 ppm H_2S belies the excursions to >60 ppm.

Figure 6. Case Study 1: Baseline H_2S profile (2 day graph)

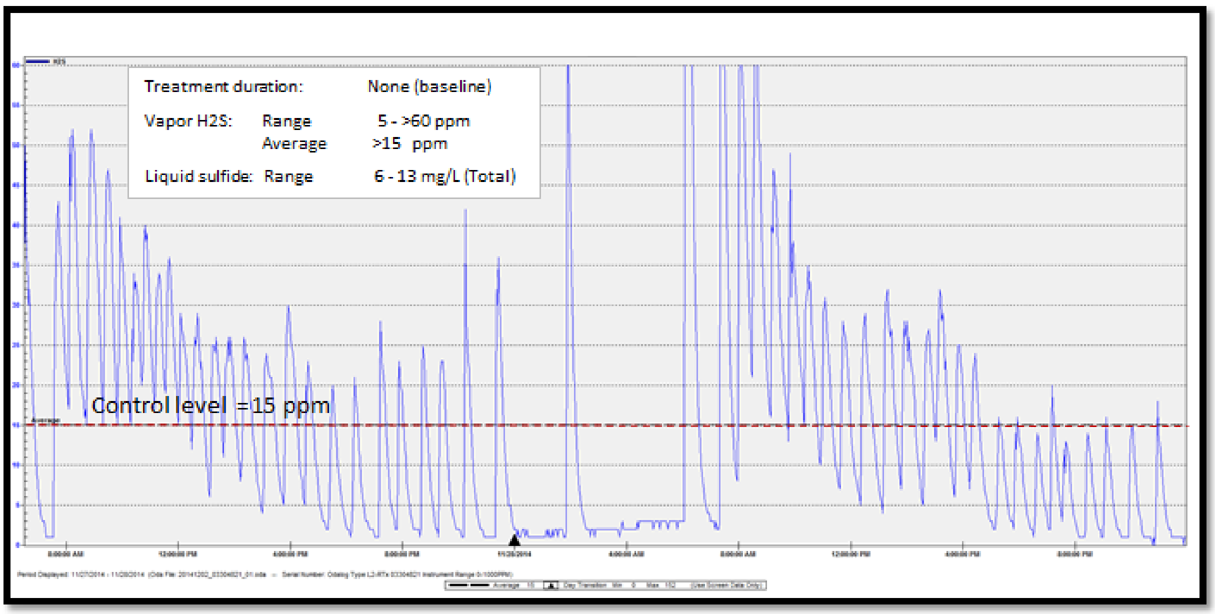


Figure 7 shows the H_2S readings through the first 13 days following the initial 24-hr Cloevis treatment. The results show a 3-4 day period where H_2S production is completely suppressed, followed by a slow recovery to where H_2S control levels began to be exceeded on Day-8.

Figure 7. Case Study 1: Conditioning-phase Cloevis treatment (13 day graph)

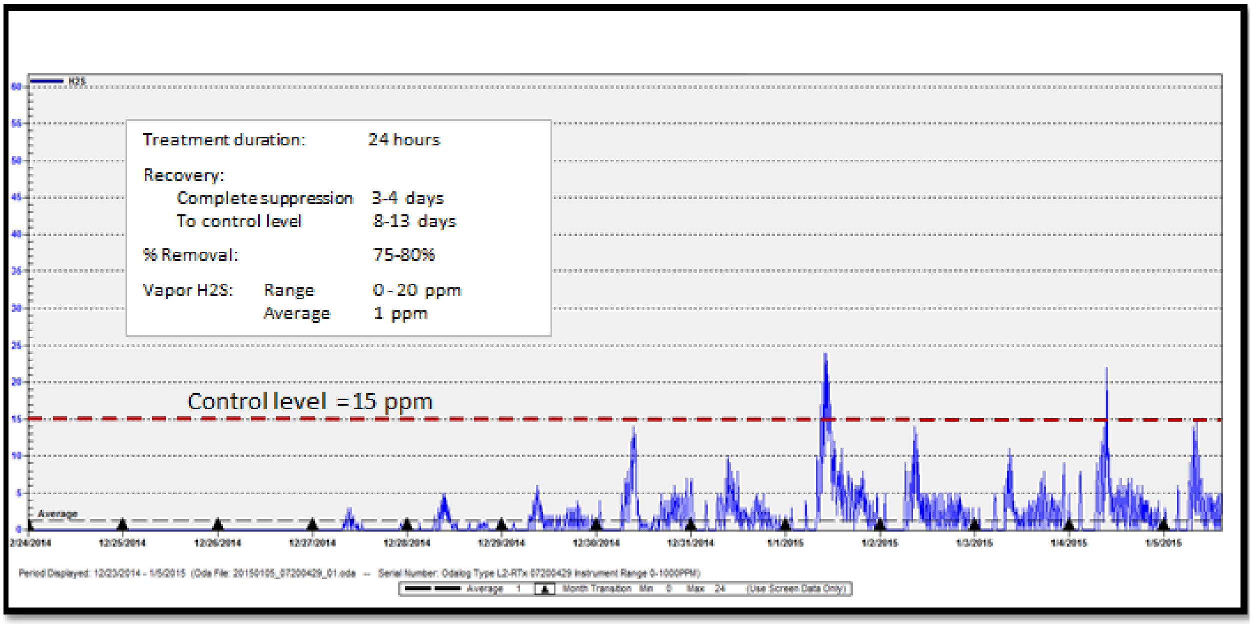
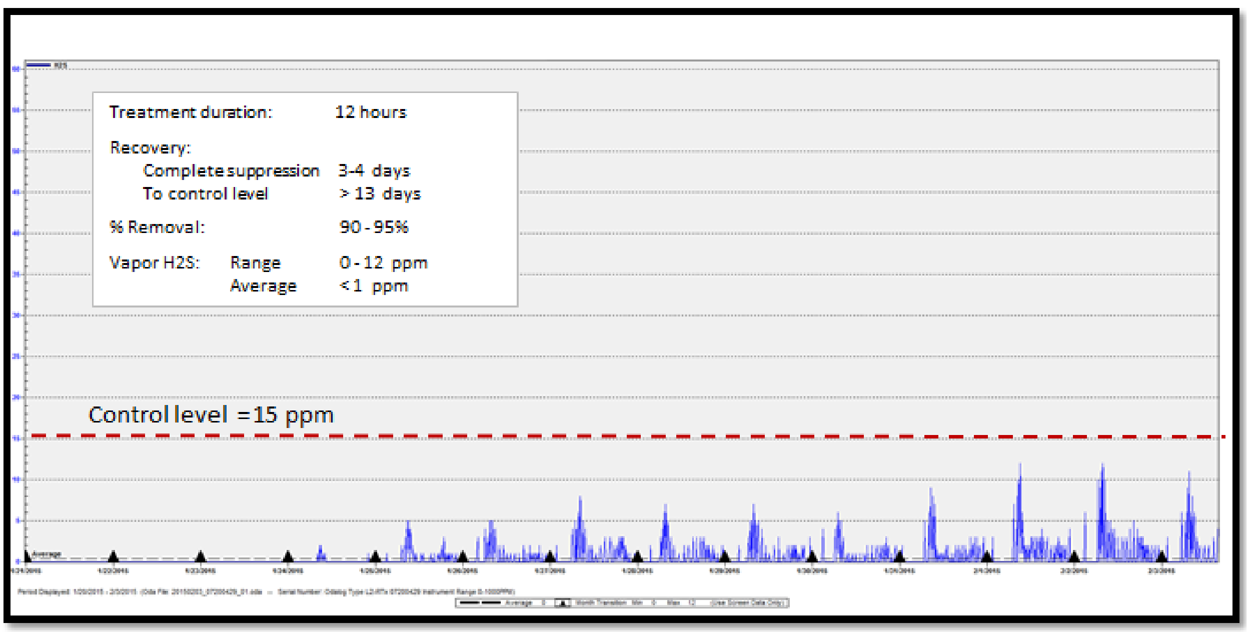


Figure 8 shows the H_2S readings following a subsequent maintenance treatment. These results show continued control beyond the 13 day datalogging period (extending to 18-21 days).

Figure 8. Case Study 1: Maintenance-phase Cloevis treatment (13 day graph)



Case Study 2

Force main length .... 3,200 feet
Force main diameter .... 10 inches
Force main retention time .... 1 - 2 hours
Wastewater flow .... 0.95 MGD

The second case study, like the first, involved a straightforward application where there was no prior treatment, but this second case afforded the opportunity to compare Cloevis to continuous nitrate dosing.

Figure 9 shows the baseline vapor H_2S readings over a 12-day period at the force main discharge. In this case, H_2S levels were significantly higher than the control level, even through the low-flow early AM hours.

Figure 9. Case Study 2: Baseline H_2S profile (12 day graph)

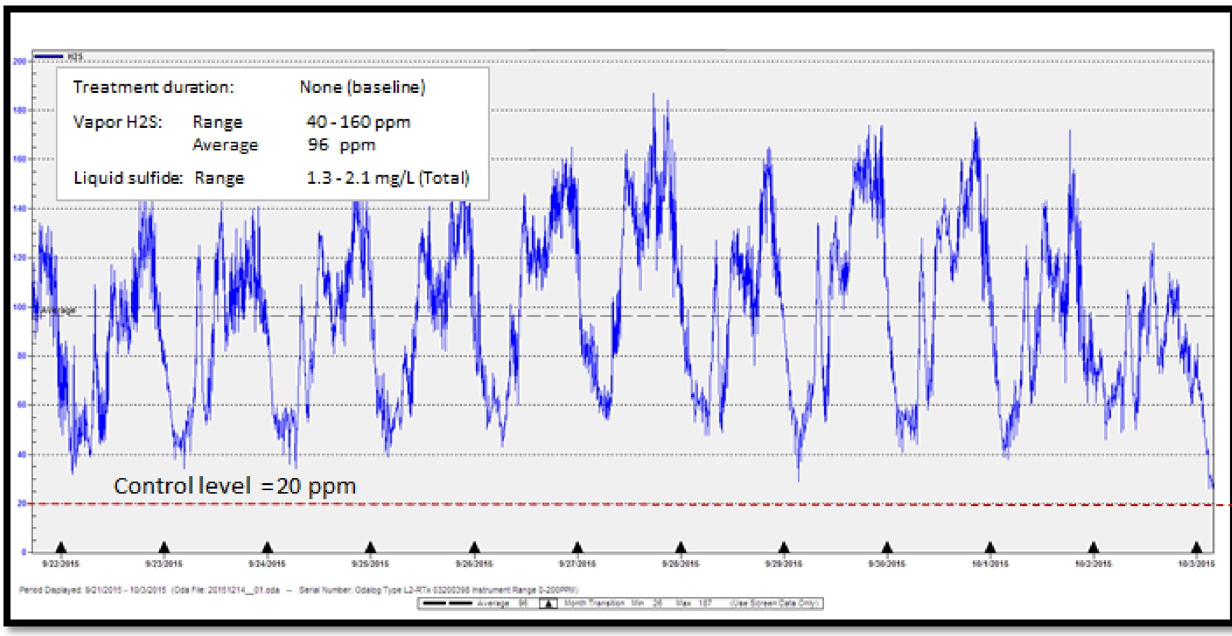


Figure 10 shows the results obtained by dosing nitrate at a rate of 29 gpd, or a ratio of approx. two gallons per lb-Sulfide. The effect was a substantial 80-90% reduction in H_2S at the FM discharge, though there remained several hours of the day where control levels were exceeded by a factor of two or more. Increasing the nitrate feed rate to 39 gpd was able to consistently control H_2S to the target level (Figure 11).

Figure 10. Case Study 2: Nitrate treatment 29 gpd (9 day graph)

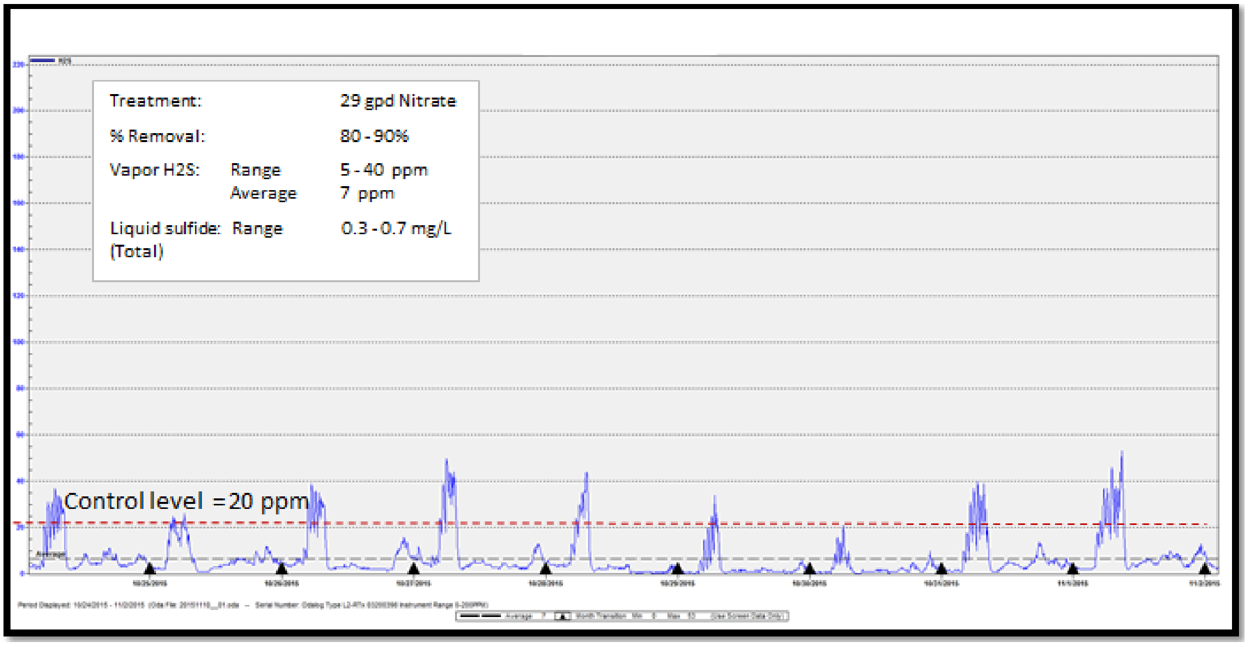
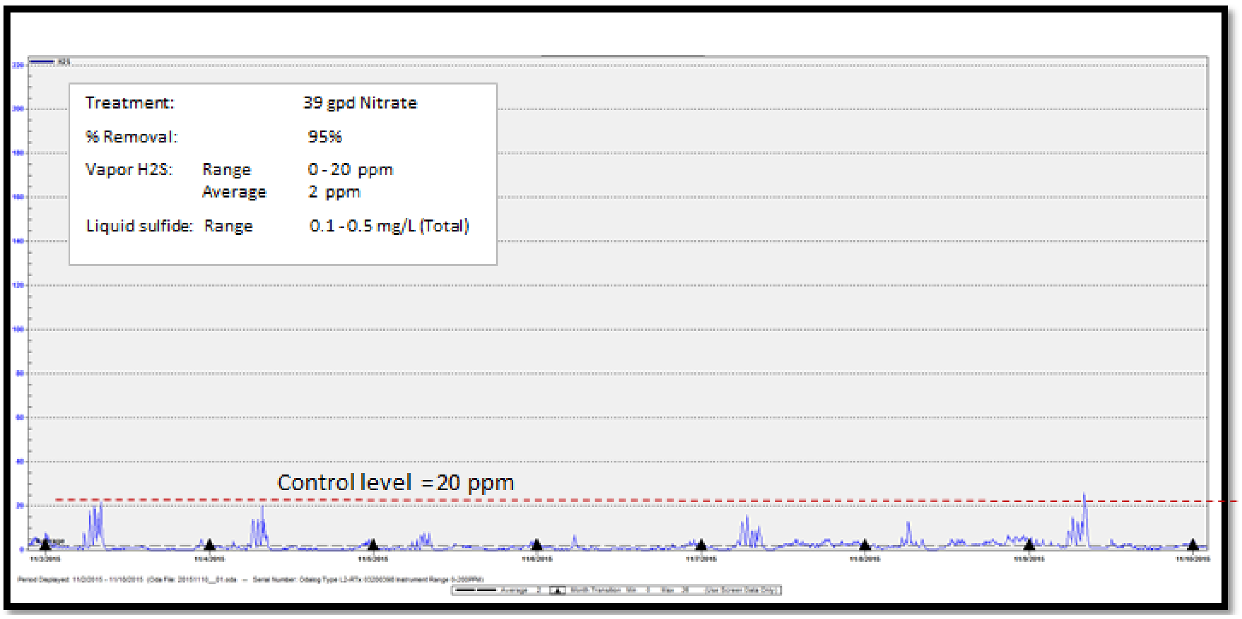


Figure 11. Case Study 2: Nitrate treatment 39 gpd (7 day graph)



Results following the initial two Cloevis treatments are shown in Figures 12 and 13. The first treatment resulted in complete H_2S suppression for 4-6 days, with the 20 ppm control level sustained for over 13 days (Figure 12). Results following a second (shorter) Cloevis treatment extended the length of complete suppression to 9-10 days, with control levels sustained for 18 days (Figure 13).

Figure 12. Case Study 2: First Cloevis treatment (13 day graph)

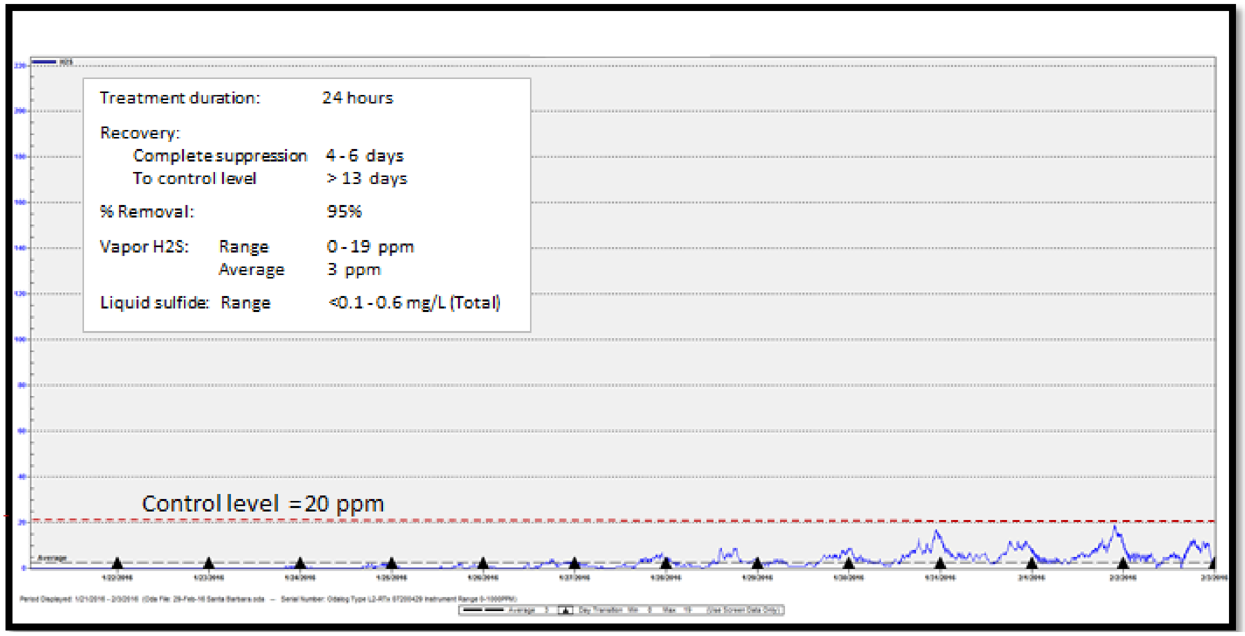
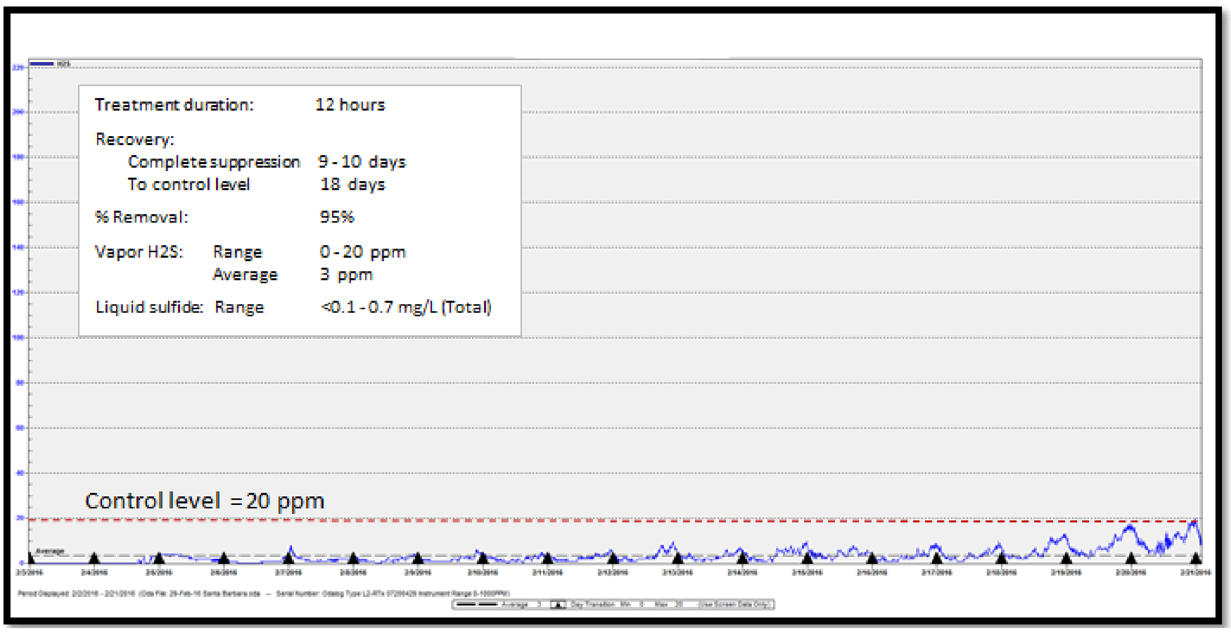


Figure 13. Case Study 2: Second Cloevis treatment (18 day graph)



<u>Case Study 3</u>

Force main length	8,600 feet
Force main diameter	8 - 10 inches
Force main retention time	4 - 6 hours
Wastewater flow	0.13 MGD

The third case study was more challenging in that retention times were longer and there was a manifolded force main input that comprised about 25% of the FM flow. The baseline H_2S levels over a two-day period are shown in Figure 14, and exhibit the classic diurnal pattern of low levels in the early AM hours, followed by the flush of stagnant retained wastewater, then a slow build in levels through the afternoon and into the evening. The control level in this case was 10 ppm, which meant a 90% H_2S removal target.

Figure 14. Case Study 3: Baseline 24-hr H_2S profile (2 day graph)

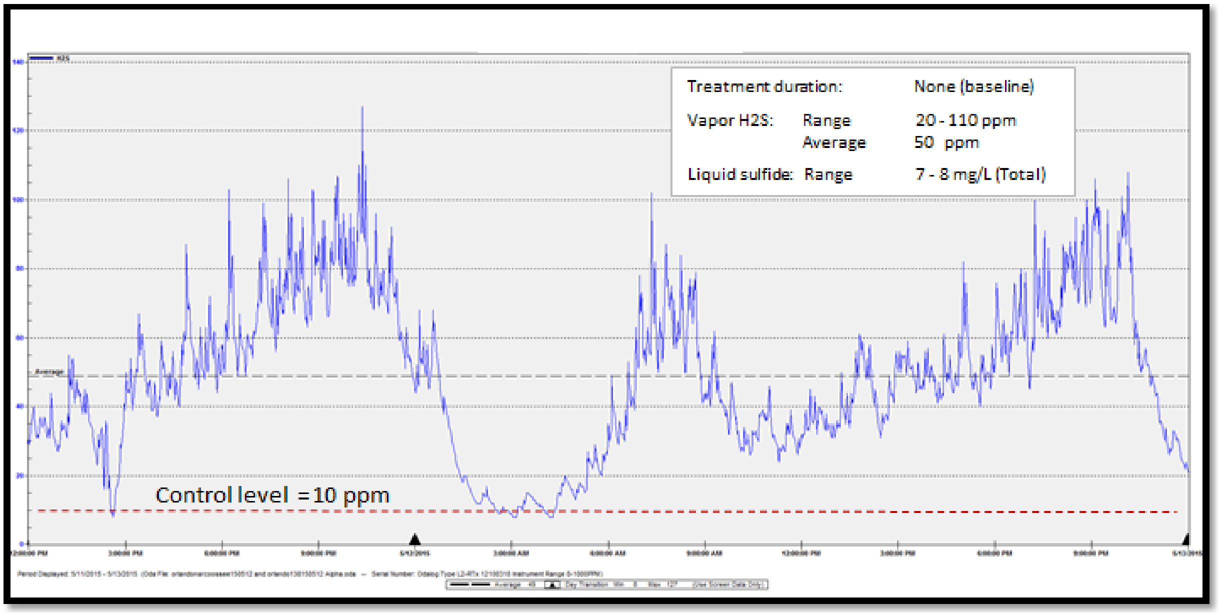
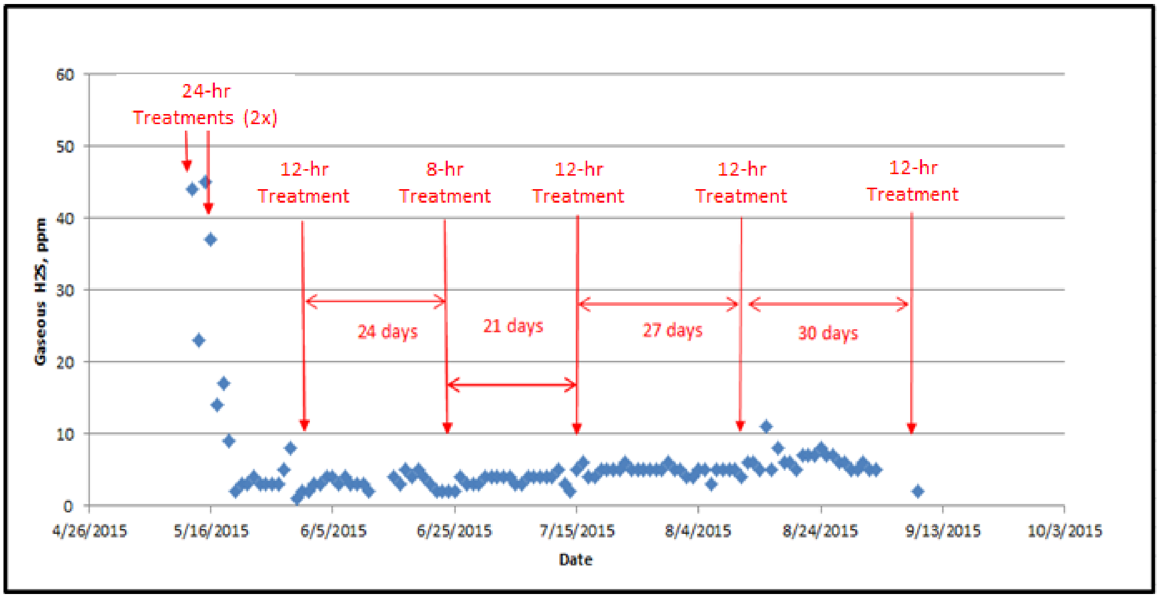


Figure 15 plots the average daily H_2S level through the entire Cloevis study, including the initial conditioning phase and subsequent maintenance phase. Two sequential treatments were needed to suppress H_2S levels to meet the control target, though a third conditioning treatment was needed to allow maintenance treatments at 20+ day intervals.

This case illustrates one of the inherent shortcomings of biofilm treatments in meeting every sulfide control need. The external contribution of pre-existing sulfide by the manifolded FM meant that, even with complete suppression of sulfide production within the target FM segment, there remained a persistent low level of H_2S at the FM discharge. Fortunately, in this case it was not of a magnitude to preclude success.

Figure 15. Case Study 3: Average daily H_2S levels though the Cloevis test (120 day graph)



Discussion

Site qualification / Preliminary assessment. Particularly in this early commercialization stage, careful attention has been paid to the data collection and analysis needed to: a) select sites for Cloevis testing; and b) streamline the initial conditioning phase, i.e., optimize the labor, equipment, chemical, and time components for this resource-intensive phase. The first-pass evaluation compares basic aspects of the prospective site to those of successfully treated sites. This is a paper exercise that looks at the physical aspects (FM size/distance, flow, and interconnecting lines) as well as general control objectives and site constraints. The second-pass evaluation involves going into the field to measure wastewater conditions (especially sulfide levels) at both the upstream pump station and downstream FM discharge, vapor dynamics at the FM discharge, and detailed design and operating information on the FM pump station. This ensures that all parties are on the same page with regard to specific objectives and constraints, and informs prescription and activities for the initial conditioning phase.

Since the key performance measure is H_2S levels at the FM discharge, of particular importance in this qualification stage is an accurate understanding of vapor dynamics at the FM discharge. Poor vapor flow is a frequent occurrence that complicates performance measurement by dampening H_2S response. Another problem is migratory H_2S that originates from a nearby gravity main discharge that, due to pressure differentials, pushes H_2S vapors upstream into the FM discharge segment.

Initial conditioning phase. The three cases discussed in this paper were fortunately straightforward in their physical/operational layout, so the initial conditioning phases went smoothly. Other sites (not reported here) were not so fortunate. These ‘difficult’ sites fall into two categories that require special conditioning procedures.

- For force mains with heavy FOG accumulation, penetration of the FNA into the SRB layer is inhibited, so several treatments may be needed before the conditioning is complete. Applying a caustic shock 1-2 days before beginning the Cloevis treatments effectively removes the FOG and accelerates the conditioning phase.

- For force mains previously treated with iron salts, FeS deposits accumulate within the biofilm and then dissociate into H_2S and Fe^{2+} at the pH 5-6 conditions needed for FNA production. If this is not anticipated and addressed beforehand, severe H_2S spikes at the FM discharge can occur during the Cloevis treatment. Special procedures have been develop to minimize this occurrence.

Ongoing operation and maintenance. Compared to the initial conditioning phase, the maintenance phase of the Cloevis technology is simple and routine – provided that the mix of labor, equipment, and chemicals was optimized during the earlier design step. The optimal mix depends primarily on the amount of flow being treated and the constraints placed on storing/feeding the Cloevis precursor chemicals. For example, onsite storage of chemicals can afford automated or remote operation of the Cloevis treatments, and so economize costs for larger wastewater flows. On the other hand, constraints for a low community profile may warrant the higher costs of a completely mobile solution where chemicals, equipment and labor are brought onsite for the Cloevis treatment and then removed upon completion of the treatment. In other situations, a combination approach may be preferred where the chemical storage/dosing equipment remains onsite but the chemicals are delivered and used for each treatment.

Complementary/Hybrid approaches. For those cases where pre-existing sulfide is entering the FM segment, some type of complementary treatment may be needed. This could be applying Cloevis to the contributing segment, or using a continuous-feed treatment chemical to control that sulfide before it enters the FM segment. For example, a low dose of H_2O_2 or nitrate into the FM wetwell can remove sulfide entering the FM segment.

Another complementary fit may be using Cloevis to remove the bulk of sulfide, and ramping up feed of a continuous-feed treatment chemical as the biofilm recovers to target H_2S levels. For example, iron salt feed could begin at Day-14 after the Cloevis maintenance treatment, and the daily feed rate could be increased as sulfide levels increase. At a predetermined maximum daily feed rate, the cost for continued increases in iron feed rate exceeds the cost for applying a Cloevis maintenance treatment. Managing such a combination to achieve least-cost performance is practical using the H_2S datalogging / telemetry and remote pump controls that are available today.

Conclusions

The Cloevis Biofilm Removal technology has been successfully scaled from the laboratory to the commercial arena. The technology has been shown to be robust and adaptable to a broad range of force main situations. The duration of control between treatments is 2-3 weeks, and no adverse downstream impacts have been observed. As biofilm treatments are fundamentally different than the more commonly used continuous-feed control chemicals, careful attention must be paid to designing a Cloevis application. More critical still are the considerations for integrating Cloevis into a broader, system-wide sulfide control program. These challenges are simplified by providing the technology as a service. Consequently, a commercial delivery vehicle has been developed by USP Technologies that assures performance and requires no capital or labor by the customer. Provided as such a service, the effective cost of the Cloevis technology is competitive with continuous chemical feed alternatives such as nitrate and iron salts.

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