

A Novel Test Method for Measurement of MIC in a Wastewater Collection System

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ABSTRACT

Microbial Induced Corrosion (MIC) in wastewater collection and treatment systems is a severe and on-going problem in the United States. A 1991 United States Environmental Protection Agency (USEPA) report to congress cites a national cost, in 1991 dollars, for sewer rehabilitation at \$6 billion (Bowker et al, 1991). In addition to the direct cost of replacing corroded infra-structure, there are hidden costs in lost time and labor which are diverted to emergency and repair activities, and thus are not spent on core wastewater collection system operations. Evoqua engaged in a study to determine the impact of hydrogen sulfide concentration on the strength and integrity of concrete in wastewater collection systems. Concrete test samples were deployed at the discharges of two force mains for two years. Both force mains were similar in terms of potential for sulfide generation and hydrogen sulfide release. One site was treated with a nitrate double salt solution to prevent the formation of sulfide in the wastewater, while the other was left untreated. Concrete test samples were compared at six-month intervals to assess the impact of hydrogen sulfide gas on the strength and integrity of the material. After two years of exposure in a manhole conveying an untreated stream, the concrete samples were exposed to an average of 68.5 ppmv hydrogen sulfide; those samples lost 5.4% of their original mass and 13% of their original strength. The samples deployed downstream of the treated site were exposed to an average of 3.6 ppmv hydrogen sulfide, and showed a 0.2% reduction in mass and a 9% increase in compressive strength. The primary conclusion from the trial is that minimal corrosion of concrete occurred at hydrogen sulfide concentrations below 5ppmv.

KEYWORDS: Collection system, corrosion, concrete, hydrogen sulfide

INTRODUCTION

A 1991 USEPA report to Congress outlines the severity and impact of concrete corrosion as surveyed by County Sanitation District of Los Angeles County (CSDLAC). Of 89 cities participating in the survey, 32 cities reported sewer collapses of which 81% of the collapses are believed to be due to hydrogen sulfide corrosion. Furthermore, the study indicated that almost 70 percent of the 61 respondents experienced hydrogen sulfide corrosion at the treatment plant.

“...sewer systems suffering from hydrogen sulfide corrosion generally require costly, premature replacement or rehabilitation of pipes, manholes, lift stations, and pump stations...”ⁱ

The purpose of this study was to examine the impact of hydrogen sulfide induced corrosion on concrete in wastewater collection system. The compressive strength and mass loss of concrete corrosion specimens exposed to high levels of atmospheric sulfide (>65 ppmv) was compared to specimens exposed relatively low (<5ppmv) atmospheric sulfide levels.

Concrete Corrosion

The primary mechanism responsible for corrosion of sewers and concrete structures used in the conveyance and treatment of sewage is acid attack resulting from the biological conversion of hydrogen sulfide gas to sulfuric acid in the presence of moisture. The corrosion process is defined US EPA Doc 430/09-91-09 (1990) and Joyce (2000) along the following progression:

1. Under anaerobic conditions, anaerobic bacteria such as *Desulfovibrio desulfuricans*, reduce naturally present sulfate to sulfide in the bulk wastewater. Sulfate reducing bacteria such as *desulfovibrio desulfuricans* naturally occur in municipal wastewater collection and treatment systems. They are obligate anaerobes which utilize sulfate as a hydrogen acceptor and a variety of organic matter as a hydrogen donor.
2. Sulfide ions combine with hydrogen ions to form hydrogen sulfide, which exists as a gas dissolved in the water.
3. Hydrogen sulfide gas is released from the wastewater to the sewer atmosphere. The escape of hydrogen sulfide gas from solution increases with temperature due to decreased gas phase solubility. Hydrogen sulfide gas release is also accelerated by turbulent conditions.
4. Released hydrogen sulfide gas is oxidized by *Thiobacillus* bacteria to form sulfuric acid. Many species of the *Thiobacillus* genus are naturally occurring in the wastewater system and can live in a pH environment below 4.
5. Sulfuric acid reacts with calcareous aggregate (limestone) at the concrete surface to form gypsum (CaSO_4), a soft corrosion product. Soft corrosion products are easily washed away by the scouring action of wastewater flow to expose more surface area for the reaction to continue.

Factors Affecting Concrete Corrosion

Concrete corrosion of a wastewater collection system depends on many factors as pointed out by Joyce (2000). The amount of turbulence, airflow, wetted surface, wastewater chemistry, system temperature, and scouring flow all contribute to the presence of hydrogen sulfide and sulfur oxidizing bacteria. It is not in the scope of the paper to correlate an exact corrosion rate to a given hydrogen sulfide concentration, but to identify a testing method valid for other key areas of wastewater collection systems and to provide a general correlation of hydrogen sulfide presence to system corrosion.

Corrosion proof materials such as PVC and vitrified clay are available for wastewater collections systems. Concrete is widely used in the US for large diameter underground wastewater transfer. One survey (EPA 430/09-91-09) indicated that over 90 percent of cities sampled used unlined, reinforced concrete pipe (RCP) in portions of their collections system. A method for preventing corrosion in the collection system for RCP is to short-circuit the first step in the above process through treatment of the wastewater to either prevent sulfides from forming or removing existing sulfides.

Corrosion and Sulfide Control

For this study an odor control product capable of both preventing the formation of sulfides and capable of removing existing sulfides was dosed into the wetwell of the pump station. The method by which sulfides are controlled is described further in the following section.

METHODOLOGY

The process for the study is summarized as follows:

1. Two similar wastewater collection systems were located; one was treated with sulfide controlling chemical and the other was left untreated.
2. Sulfide control product was dosed into the treated site.
3. Background information was gathered on both collection systems.
4. A licensed 3rd party was engaged to act as concrete sample manufacturer and tester.
5. A batch of 16 concrete samples was split and deployed at the forcemain outfalls of the two collection systems.
6. Continuous hydrogen sulfide monitoring was performed, and monthly wastewater chemistry was sampled.
7. At least two concrete samples were retrieved from each location every 6 months for washing, weighing, and strength testing.

Summary of Study Sites

The following criteria for selecting sites for the study were used:

- Both sites had to be stable without any expansion or construction work planned for the duration of the study.
- Both sites had to be in close proximity to ensure similar seasonal and environmental factors including hydrogen sulfide potential, ambient temperatures, humidity and wastewater chemistry.
- Both sites had to be similar in factors that lead to production and release of hydrogen sulfide, these are generally accepted to include:
 - Forcemain Dimensions
 - Wastewater Retention Time
 - Biological Oxygen Demand
 - Wastewater Temperature
- Both sites had to be readily accessible for sampling and sulfide control chemical dosing and delivery.
- The un-treated site and associated forcemain had to be tolerant of odors resulting from the emission of hydrogen sulfide in higher concentrations.

Two suitable sites were located within the collection system of a single municipality. The sites were located within 12.2 km of one another. An illustration of the collection system segments is provided in figure 1. A summary of the sites is presented in table 1

Figure 1. Diagram of untreated (left) and treated (right) wastewater collection systems.

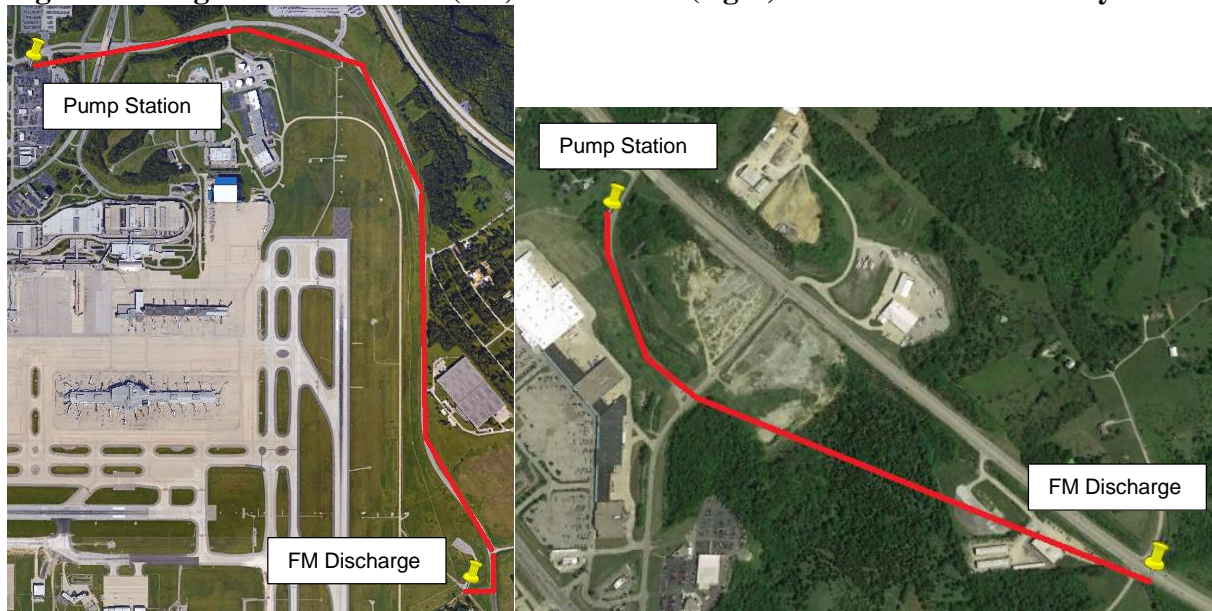


Table 1 – Collection System Characteristics

Parameter	Untreated PS	Treated PS
Average Daily Flow (ML/d)	0.723	0.416
Forcemain Length (m)	2,993	1,341
Forcemain Diameter (cm)	15.2	20.3
Average Retention Time (hr)	1.8	2.5

Sulfide Control Method

A nitrate based product chemistry was selected for hydrogen sulfide control for the following reasons:

- It has demonstrated effective sulfide control at other sites within the municipality’s treatment area.
- It is well suited for sulfide control in wastewater collection systems with anaerobic retention times greater than 2 hours.
- It is safe to handle as it is a non-hazardous chemical.
- It is easy to feed through positive displacement pumps very accurately.
- Nitrate can be tested very quickly downstream and measure to indicate if the correct amount of product is applied for hydrogen sulfide elimination.

Evoqua Water Technologies supplied Bioxide[®] as the calcium nitrate based product for use in this corrosion rate study. Bioxide[®] contains 420g of nitrate oxygen per liter. It is used safely and effectively in over one hundred municipalities to control hydrogen sulfide related odors and corrosion on a daily basis.

The odor control product was added into the wetwell of the pump station upstream of the control point. Dosing was set at a rate of 5 liters per hour. The feed equipment was manufactured by

Evoqua Water Technologies to allow precise product feed. The product feed and storage system used to meter chemical into the wastewater is shown in figure 2.

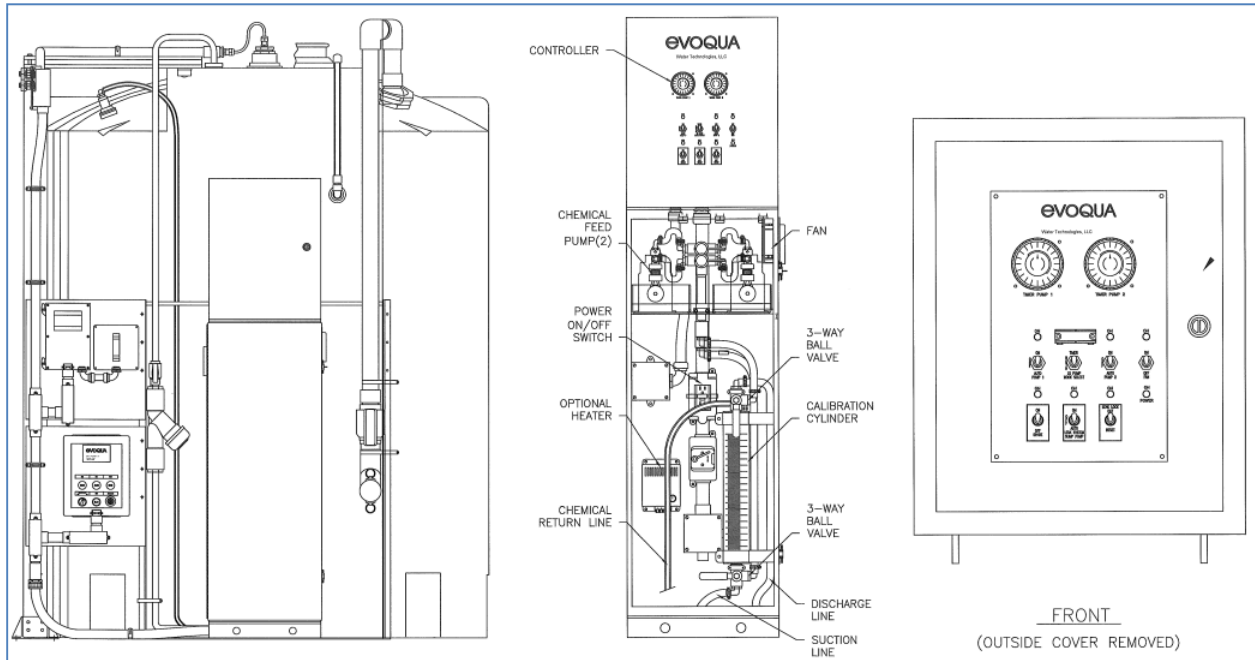


Figure 2 – Sulfide Control Chemical Feed System

Concrete Test Specimens

The concrete test specimens were created by a 3rd party manufacturer in accordance with specifications outlined in ASTM C150 – “Standard Specifications for Portland Cement”. The specimens were constructed of Type II Portland cement following the standard practice for making and curing concrete test specimens in the laboratory as designated under ASTM C192. Type II Portland cement is suitable for general use where moderate sulfate resistance is desired. This type of concrete is normally specified by engineering firms in the northern Kentucky area for construction of wastewater structures.

After manufacture of specimens was complete, and upon the semi-annual retrieval of test specimens from the field, each concrete cylinder was pressure washed utilizing a 25° angle spray head at flow rate of 2-3 gpm and unknown pressure. The purpose of the wash was to remove soft calcium sulfate corrosion product from the surface of specimens. Both specimens were washed in an equal manner for an equal comparison in final weight.

Each sample was labeled for future reference and weighed on a digital laboratory balance which was calibrated using a standard mass, and with an accuracy of +/- 10 grams. The balance used was an CD Industrial Indicator balance (CD11) as manufactured by Ohaus of Parsippany, NJ.

Following the measurement of the remaining mass of the concrete specimens, they were subjected to compressive strength testing as outlined in ASTM C39.

A compressive axial load was applied to the molded cylinders, at a rate prescribed under the aforementioned standards, until failure occurred. The compressive strength of the specimens was calculated by dividing the maximum load attained during the test by the cross-sectional area of the specimen.

The compressive strength testing was performed by Consulting Services Incorporated of Kentucky, an independent 3rd party consultant certified for performing concrete integrity testing as outlined in ASTM C39. The diameter, area, maximum load in pounds, and the type of failure were reported. The testing equipment used was a FHS Series Premium Compression Tester, manufactured by Forney of Zelienople, PA.

Field Testing

At the locations where the concrete specimens were deployed several parameters in the liquid and in the vapor above the wastewater were collected. These were dissolved sulfide concentration, pH, and sulfide control chemical residual from the liquid, and atmospheric hydrogen sulfide. A brief summary of each parameter, the method of collection and associated equipment is provided below.

Atmospheric hydrogen sulfide was measured in the air space adjacent to the concrete samples at the location of the force main outfall. An Odalog[®] Type RTx hydrogen sulfide monitor with extended life sensor was used. The Odalog[®] Type RTx is manufactured by App-Tek of Australia, and distributed by Detection Instrument of Arizona. The monitor was programmed to record atmospheric sulfide readings at 5 minute intervals. The monitor contained an integral cellular modem capable of uploading data to a website on a pre-programmed basis. The data logger was calibrated and replaced with a fresh monitor on a 60-day rotation.

Dissolved Sulfide concentrations were measured at the discharge of the forcemain. A Sulfide Test Kit was used manufactured by LaMotte of Chestertown, MD. The basis for the test is outlined under section 4500-S²⁻ of the standards published by the American Public Health Association, AWWA, and WEF. The range for the test is from 0 to 18 mg/L with an accuracy of 0.1mg/L. The tests were generally performed on a monthly basis to assess atmospheric sulfide generation potential and to optimize sulfide control chemical dosing rates.

The pH of the wastewater was monitored on a regular basis using a heavy duty pH meter manufactured by Extech Instruments of Nashua, NH. The meter was calibrated on a daily basis. pH measurements were generally taken once per month to establish hydrogen sulfide release potential.

Nitrate residual was measured to optimize the economy of feeding sulfide control product at the treated site. The tests were performed using a nitrate/nitrite test strips manufactured by Aquachek of Elkhart, IN. The nitrate residual was measured seasonally.

Liquid samples were collected on a monthly rotation.

DATA

Average atmospheric sulfide at the treated location was 3.6 ppmv. Average atmospheric sulfide at the untreated location was 68.5 ppmv. The municipality came under budgetary constraints during the early part of 2013. Dose rates at the treated site were reduced by 44% February through May of 2013 compared to the chemical use rates in 2012. As a result the municipality saved a little more than \$3,000 in product at this site, however atmospheric sulfide concentrations were about 10x higher, and dosing levels in July of 2013 were resumed at previously established summer rates to provide improved odor control at the emission point.

Atmospheric Hydrogen Sulfide

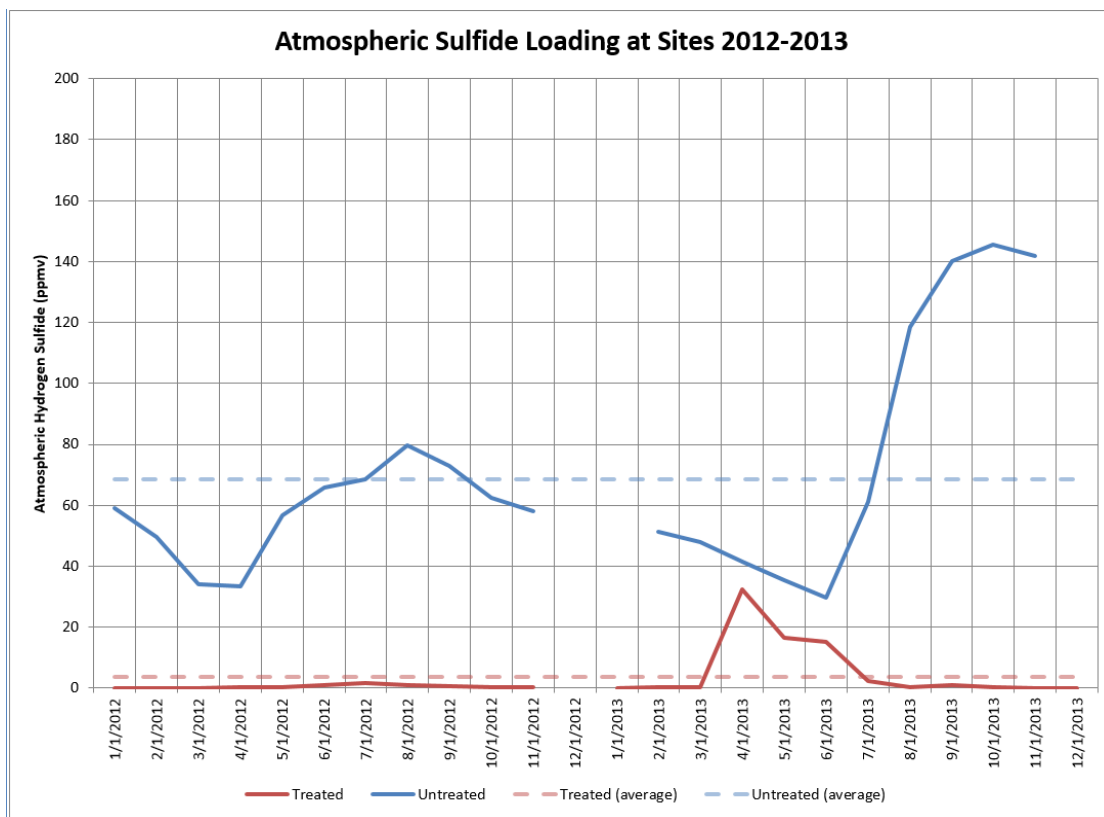


Figure 3– Atmospheric Hydrogen Sulfide Concentrations at Concrete Specimen Deployment Sites

Table 2 - Atmospheric Hydrogen Sulfide Concentrations at Concrete Specimen Deployment Sites

	Treated Atmospheric Sulfides (ppmv)		Untreated Atmospheric Sulfides (ppmv)	
	2012	2013	2012	2013
January	0.0	0.1	59.2	N.D.
February	0.0	0.1	49.8	51.4
March	0.1	0.1	34.1	47.8
April	0.3	32.3*	33.5	41.6
May	0.2	16.5*	56.6	35.3
June	1.1	15.2*	65.8	29.7
July	1.5	2.4	68.7	61.2
August	1.1	0.2	79.5	118.5
September	0.7	0.9	72.9	140.2
October	0.3	0.3	62.6	145.5
November	0.3	0.0	58.2	141.7
December	N.D.	0.0	N.D.	N.D.
AVERAGE	3.6		68.5	

* - Dose Rate Reduction in Response to Budgetary Cost Reduction Measures

N.D. – No Data

The table above shows a 95% lower atmospheric sulfide concentration at the site where sulfide control chemical is dosed upstream compared to the untreated site.

Total Dissolved Sulfide Concentration

Dissolved sulfide measurements were taken at both locations on a monthly basis. The purpose of measuring the sulfide content on the water is to quantify the total mass of sulfide in the wastewater stream. The total mass of sulfide per day combined with chemical residual, form the basis for dose rate optimization of sulfide control chemical. Experience has shown that dissolved sulfide concentrations are the most important factor in determining the potential for hydrogen sulfide release to atmosphere.

The dissolved sulfide concentration at the treated site average less than 0.1mg/L, with a peak concentration of 0.5mg/l occurring during the aforementioned budgetary cost savings measures implemented during the spring of 2013.

At the untreated location average dissolved sulfide concentrations were 89 times higher than at the location where sulfide control chemical was dosed upstream.

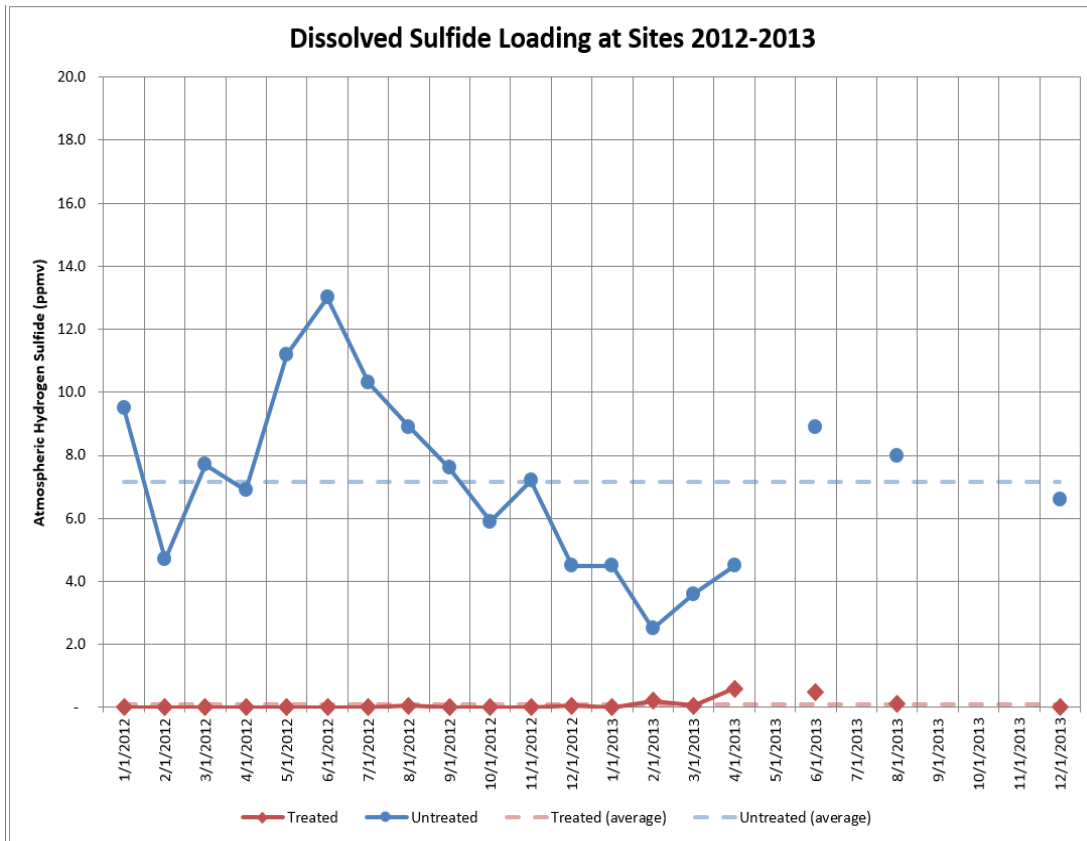


Figure 4– Dissolved Sulfide Concentrations at Concrete Specimen Deployment Sites

Table 3 - Dissolved Sulfide Concentrations at Concrete Specimen Deployment Sites

	Treated		Untreated	
	2012	2013	2012	2013
January	0	0	9.5	4.5
February	0	0.2	4.7	2.5
March	0	0.05	7.7	3.6
April	0	0.6	6.9	4.5
May	0		11.2	
June	0	0.5	13	8.9
July	0		10.3	
August	0.05	0.1	8.9	8.0
September	0		7.6	
October	0		5.9	
November	0		7.2	
December	0.05	0	4.5	6.6
AVERAGE	0.08		7.16	

pH

The wastewater downstream of the untreated forcemain showed on average a pH that was 0.5 units higher than that of the treated line; it averaged 7.9 standard units compared to 7.4 units. The difference in pH levels is not fully understood, but it is likely a result of runoff and wastewater characteristics of the nearby airport. The pH of the treated site was slightly above the normal range for wastewater.

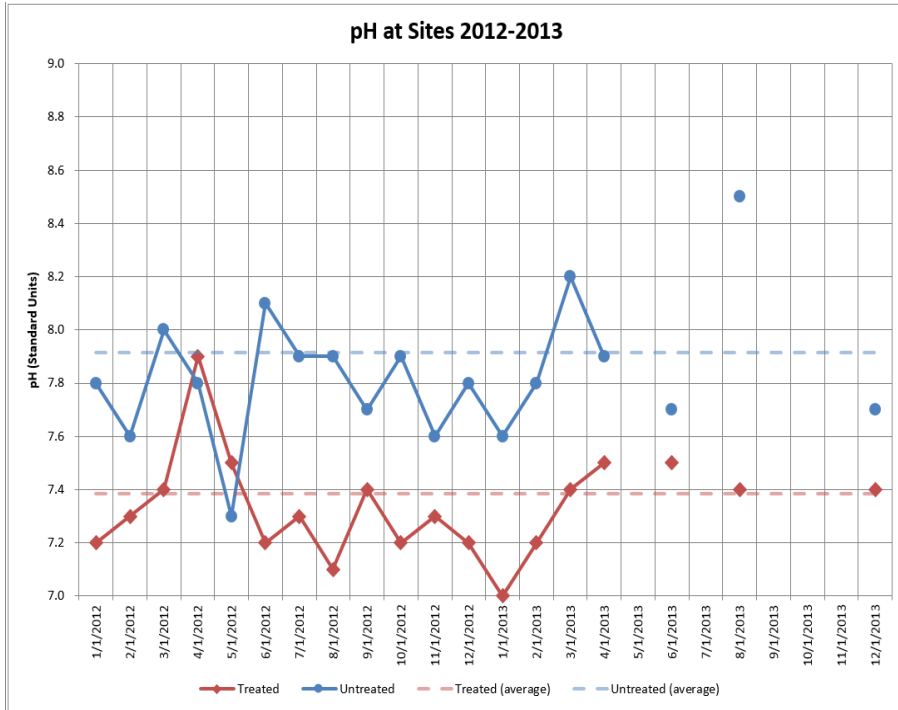


Figure 5 – Wastewater pH at Concrete Specimen Deployment Sites

Table 4 – pH at Concrete Specimen Deployment Sites

	Treated		Untreated	
	2012	2013	2012	2013
January	7.2	7.0	7.8	7.6
February	7.3	7.2	7.6	7.8
March	7.4	7.4	8.0	8.2
April	7.9	7.5	7.8	7.9
May	7.5		7.3	
June	7.2	7.5	8.1	7.7
July	7.3		7.9	
August	7.1	7.4	7.9	8.5
September	7.4		7.7	
October	7.2		7.9	
November	7.3		7.6	
December	7.2	7.4	7.8	7.7
AVERAGE	7.4		7.9	

Sulfide Control Chemical Application Rates

A calcium nitrate double salt solution was dosed into the wet well upstream of the treated control point. The chemical dose rate was adjusted on a seasonal basis throughout the year based on dissolved sulfide concentration and nitrate residual gathered at the control point. Chemical dose rates were reduced by 44% from February – May of 2013 in response to budgetary constraints. Nitrate/nitrite residual strips were used to estimate the amount of un-reacted chemical present downstream of the application point.

A slight residual (< 5mg/l) was recorded during every month with exception of the aforementioned budget mediated months. For each month where a residual was measured, there was no detectable dissolved sulfide concentration and atmospheric averages did not exceed 1.5 ppmv.

The average residual of 2.4 mg/L of nitrate plus nitrite nitrogen represents an over feed of about 6.8 liters per day, or approximately 5.6% more chemical than the system demands for 100% efficiency.

Table 5 – Sulfide Control Application Rates

	Feed Rate (L/d)		Chemical Residual (mg/L)	
	2012	2013	2012	2013
January	129	123	2	4
February	113	62	4	0
March	108	64	4	0
April	114	61*	4	0
May	108	66*	3	
June	117	136	1	0
July	158	137	2	
August	173	126	2	4
September	137	124	3	
October	132	178	4	
November	131	178	2	
December	129	103	4	3
AVERAGE	121		2.4	

CONCRETE TEST SPECIMEN DATA

The specimens were deployed in corrosion resistant nylon mesh bags and tethered to the concrete side of the control point manhole with stainless steel cables. A visual inspection of the specimens was performed monthly while gathering data at the manhole and two samples from each location were retrieved for laboratory testing every six months. The test samples were hung at the same depth in the manhole as the atmospheric sulfide monitors.

Weight Change of Concrete Test Specimens

The concrete test specimen exposed to an average of 68.5ppmv lost on average 0.73kg (5.4%) of its weight over the course of the 24 month study. The weight loss over the course of the study was linear ($R^2=0.995$) with an average loss of 0.23% per month. The specimens deployed at the site treated with sulfide control product lost on average 0.045kg (0.2%) of their original weight over the course of the study.

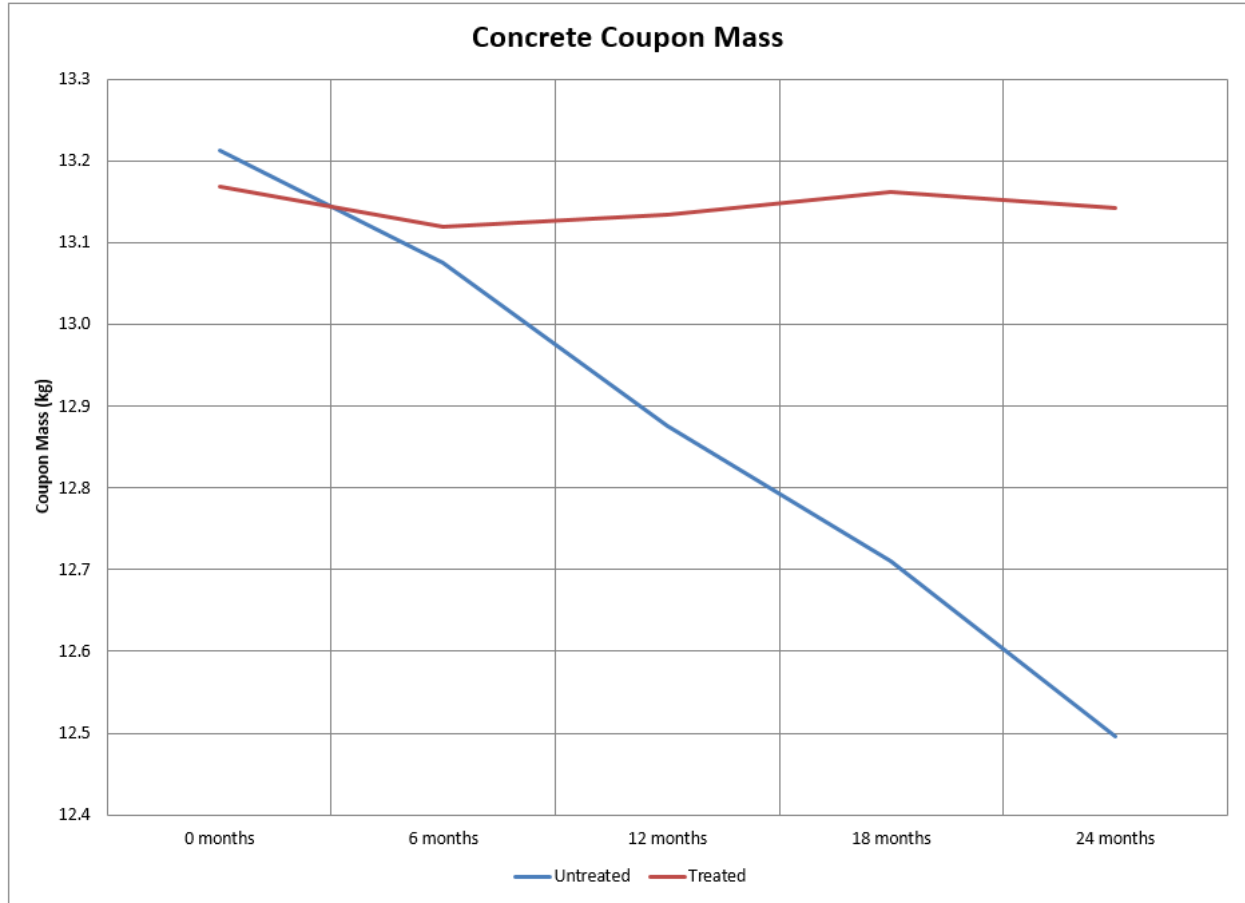


Figure 6 – Concrete Weight Loss as a Result of Sulfide Induced Corrosion

Table 6 – Concrete Weight Loss as a Result of Sulfide Induced Corrosion

	Treated		Untreated	
	Weight (kg)	% Mass Lost	Weight (kg)	% Weight Lost
0 months	13.17	-	13.21	-
6 months	13.12	-0.4%	13.08	-1.0%
12 months	13.14	-0.3%	12.88	-2.6%
18 months	13.16	-0.1%	12.71	-3.8%
24 months	13.14	-0.2%	12.5	-5.4%



Figure 7 – Treated Samples (back) showing 0.3% mass loss after 12-months compared to untreated Sample (front) showing 2.6% mass loss.



Figure 8 – Untreated Sample after 18-months showing a little more than 500grams of concrete loss



Figure 9 – Treated Sample (left) and untreated (right) after 24-months showing corrosion of concrete.

Compressive Strength Change of Concrete

Hydrogen sulfide induced corrosion was measured in this study in two ways. Table 6 above shows data for the loss in mass. Figures 7, 8 and 9 clearly show a difference in the concrete samples from exposure to hydrogen sulfide versus the control. Figure 10 and Table 7 below present the results of compressive testing.

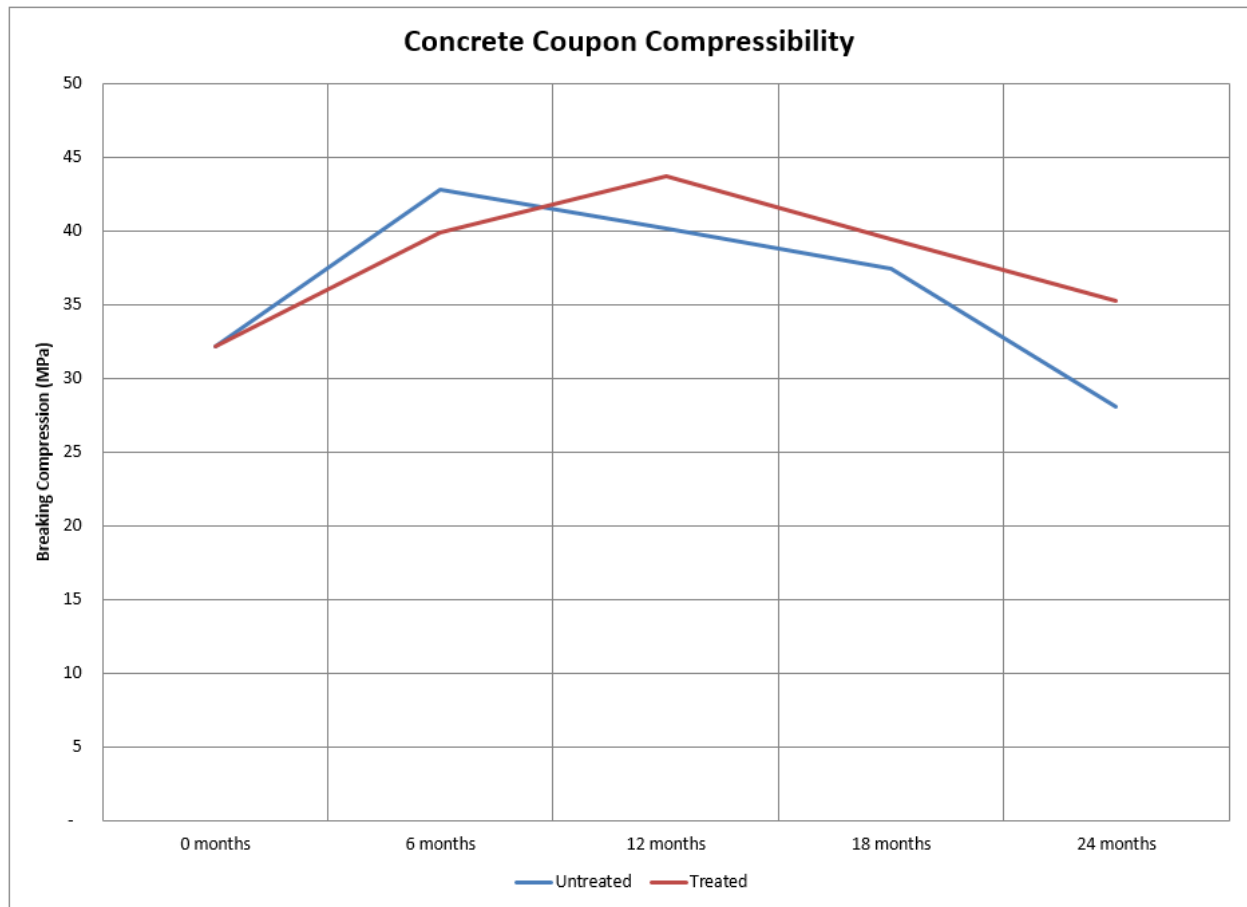


Figure 10 –Weakening of Compressive Strength as a Result of Corrosion

Table 7 – Weakening of Compressive Strength as a Result of Corrosion

	Treated		Untreated	
	Compressive Strength (MPa)	% change relative to original Strength	Compressive Strength (MPa)	% change relative to original Strength
0 months	32	-	32	-
6 months	40	+24%	43	+33%
12 months	44	+36%	40	+25%
18 months	39	+23%	37	+16%
24 months	35	+9%	28	-13%

DATA DISCUSSION

The data establish a clear differentiation between the condition of concrete samples at high and low atmospheric sulfide loadings in terms of compressive strength and material loss.

The data also shows a few additional points of interest:

- A dose rate reduction at the treated location of 44% resulted in similar atmospheric hydrogen sulfide levels in April and May (24.4ppmv) as the untreated location during the same period (38.4ppmv.) Therefore control points must be diligently monitored and feed rates adjusted in order to effectively control corrosion.
- Despite the pH level at the untreated control point being 7.9 units compared to a level of 7.4 at the treated location, the elevated pH alone was not enough to prevent hydrogen sulfide from releasing into the atmosphere.
- The concrete showed a continued strengthening for a period of 6-12 months after the initial 28-day curing period. This has been documented in various sources as being a normal and standard property of Portland cement as it continues to hydrate.

Conclusion

Treating wastewater to maintain average total dissolved sulfide concentration less than 0.1 mg/l and average atmospheric sulfide concentration less than 5ppmv results in minimal corrosion effect on the strength and weight of concrete specimens. When total dissolved sulfide concentrations are allowed to reach more than 7 mg/l then, even at average pH levels of 7.9 units, atmospheric sulfides may average 68.5ppmv and concrete corrosion is observed.

When cylindrical concrete samples are exposed to an average atmospheric sulfide concentration of 3.6ppmv over two years there is negligible mass loss and no net decrease in compressive strength, however if the same samples are deployed at a similar location where atmospheric sulfide concentrations are allowed to read 68.5 ppmv then the net mass loss of the cylinder is 5.4%. The concrete cylinders exposed to the higher atmospheric sulfide concentration also experienced a decrease in compressive strength of about 13%.

Controlling sulfide production in the wastewater and hydrogen sulfide release decreases the potential for concrete corrosion.

TOPICS FOR FURTHER STUDY

Continued study of the mechanism of hydrogen sulfide induced corrosion of common building materials used in wastewater treatment and conveyance structures is warranted. Topics which should be further examined are:

- Determination of the rate of corrosion at various atmospheric sulfide levels.
- Surface pH levels related to corrosion and atmospheric sulfide concentrations.
- The direct relationship between average atmospheric sulfide concentration and the rate of corrosion of various building materials.
- Cost benefit analysis of treating wastewater against sulfide formation and release relative to cost of structure replacement.

- Life cycle estimate revision methodology for wastewater conveyance and treatment structures under various atmospheric sulfide exposure conditions.
- Dose rate optimization strategies for reducing sulfide mitigation costs in reducing the payback period of the corrosion prevention.
- New concrete materials or additives to improve the formulation of RCP against MIC.

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