Magnesium Hydroxide Feed Reduces Odor and Provides pH Stabilization at a North Texas Municipal Wastewater Plant

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ABSTRACT

As a consequence of continuing complaints regarding odorous emissions, the Trinity River Authority Denton Creek Regional Wastewater System (DCRWS) undertook a project test systems for odor control at a Lift Station and force main in the collection system. After an initial investigation, it was determined that the long detention time in the lift station force main led to anaerobic conditions and the formation of H_2S. Magnesium hydroxide was tested for odor control at the meter station at the end of the force main. In addition to the chemical feed, a Vapex® unit, which produces a hydroxyl-ion fog, was pilot tested at a metering station both in conjunction with the chemical feed and alone. Within a day of introducing magnesium hydroxide feed at the pump station, average H_2S concentrations measured at the metering station dropped to approximately 10 ppm. The Vapex unit also reduced odor complaints.

DCRWS also introduced a magnesium hydroxide feed within the plant to test the additional benefits magnesium hydroxide can have on the biological treatment system. One of two parallel treatment trains was fed with the magnesium hydroxide slurry, while the other train was used as an untreated control. At the plant, the magnesium hydroxide slurry had no impact on the sludge volume index (SVI), but did provide excellent pH stabilization and added alkalinity to the biological treatment system to help in maintaining nitrification during high ammonia load events.

INTRODUCTION

The staff at the Trinity River Authority's Denton Creek Regional Wastewater System (DCRWS) investigated the use of magnesium hydroxide to help resolve two separate operational issues they were facing. First, odor complaints from a residential neighborhood recently built next to a meter station at the end of a long force main created a need for action. Second, a long-term drop in the pH of the influent wastewater combined with increasingly higher influent ammonia concentrations raised the concern that the nitrification treatment process could be affected. This highlighted the need for a backup source of alkalinity at the plant. Based on a comparison of chemical additives that could mitigate both issues, magnesium hydroxide was identified as a possible solution and was tested both in the force main and at the plant. This paper presents the results of these tests.

ODOR CONCERNS

The DCRWS Wastewater Treatment Plant, located in Roanoke, Texas, serves 11 north Texas cities and utility districts. The service area includes Alliance Airport and the Texas Motor Speedway. Wastewater from the area is collected in two main gravity interceptors and one pressure system called the Denton Creek Pressure System (DCPS). The DCPS serves mostly residential areas and has two lift stations. The majority of the DCPS flow is pumped from the Kirkwood Lift Station through a three-mile long force main. A second, smaller lift station also contributes flow to the force main. The Kirkwood Lift Station pumps and force main were sized for ultimate capacity, and the lift station has been historically underutilized. The low flow and the long pipeline create a situation where the detention time in the force main is approximately 24 hours. This long detention time results in the formation of odorous gases and the release of high concentrations of hydrogen sulfide at the discharge point of the force main, just upstream of the DCPS meter station. Also, hydrogen sulfide odor has been noted at air release points along the length of the force main and also at Kirkwood Lift Station.

Recently, a new neighborhood was constructed next to the meter station and the release of hydrogen sulfide at the end of the force main became a nuisance. Finding a way to resolve the odor issues became a high priority.

ALKALINITY CONCERNS

Ammonia concentration in the influent wastewater stream to the DCRWS has been increasing in recent years as development in the service area has occurred. Historically, the plant has experienced high ammonia loads, with influent concentrations above 100 milligrams per liter (mg/L), during race events at the Texas Motor Speedway. A special detention basin was constructed for use during race events to provide additional treatment capacity during these high loads. The main NASCAR race has been held in April, which falls in the winter period for the DCRWS discharge permit when the monthly average discharge ammonia concentration is 5.0 mg/L. However, a second NASCAR race event was added to the schedule in November 2005, which is included in the discharge permit's summer period when the monthly average discharge ammonia concentration is lowered from 5.0 mg/L to 2.0 mg/L. The plant staff realized that it would be a challenge to maintain the nitrification process at this lower concentration, especially in November when water temperatures are decreasing.

Also, in the last several years, the normal ammonia loads to the plant have increased significantly when the detention basin is typically not in service. The average ammonia concentration over the last three years has ranged from 25 – 30 mg/L. The 84^{th} percentile ammonia concentration over this period was 37 mg/L. At the same time, the pH of the influent wastewater has fluctuated from 7.5 down to 7.0 for periods of time. Since the specific growth rate for nitrifying microorganisms is highest in a pH range of 7.4 to 8.0, the lower pH could impact the plant's ability to maintain nitrification at the higher ammonia concentrations. The DCRWS staff identified a need to have an available source for alkalinity supplementation.

SELECTION OF MAGNESIUM HYDROXIDE

Magnesium hydroxide was selected because it met the dual needs of odor control in the collection system and alkalinity supplementation for the plant's treatment process. Magnesium hydroxide was compared to lime and caustic soda as an alkalinity source. The major advantages identified for magnesium hydroxide were:

- Magnesium hydroxide has an upper pH buffer limit of 9.0. This upper pH limit coincides with the upper pH limit in the plant's discharge permit. Caustic soda can increase the pH to the 11 – 12 range. Overdosing magnesium hydroxide would not harm the microorganisms like overdosing caustic soda.
- Unlike lime, magnesium hydroxide does not result in large volumes of sludge production. According to the manufacturer's literature, magnesium hydroxide produces a magnesium salt that is not precipitated with the sludge in the final clarifiers.
- Magnesium hydroxide is safe to handle, non-toxic and non-corrosive whereas caustic soda and lime pose hazards to treatment plant personnel.

Information from Magnesium Hydroxide Manufacturer

The following information is from Premier Chemicals, a manufacturer of magnesium hydroxide:

"In biological treatment systems, magnesium hydroxide has specific advantages over caustic soda, related specifically to its solubility and reactivity that facilitates its ease and safety of application. When added to wastewater, magnesium hydroxide has the unique chemical ability to speciate as seen below. This feature is particularly important when modifying wastewater pH and alkalinity in biologically sensitive systems.

$$\mathbf{\underset{\underline{I}}{Mg(OH)_2} \Leftrightarrow \underset{\underline{II}}{MgOH^+ + OH^-} \Leftrightarrow \underset{\underline{III}}{Mg^{+2} + 2OH^-}}$$

NITRIFICATION

Nitrosomonas

$55NH_4^+ + 76O_2 + 109\ HCO_3^- \rightarrow C_5H_7O_2N + 54\ NO_2^- + 57\ HOH + 104\ H_2CO_3$

Nitrobacter

$400NO_2^- + NH_4^+ + 4H_2CO_3 + HCO_3^- \rightarrow C_5H_7O_2N + 3HOH + 400NO_3^-$

"According to M&E, nitrifying bacteria function optimally in a pH range from 7.4 to 8.6. This pH range corresponds to a wastewater chemistry with maximum available bicarbonate alkalinity (HCO_3^-) and maximum assimilation of free biogenic carbon dioxide (CO_2) into the bicarbonate cycle. Nitrification subsequently consumes approximately 7.14 mg/L of alkalinity per 1 mg/L of ammonia biologically converted.

Property	**50% NaOH**	**30% Ca(OH)2**	**58% Mg(OH)2**
% Hydroxide	**42.5**	**45.9**	**58.3**
Solubility in Water g/100 ml	**42** **10.5 mol/L**	**0.185** **0.025 mol/L**	**0.0009** **1.5517x10-4 mol/L**
Typical Dosage $Mg(OH)_2$ 50 mg/L	**6.85 mg/100 ml** **100% soluble**	**6.35 mg/100 ml** **100% soluble**	**5 mg/100 ml** **18% soluble**
Reactive Ph Observed	**14**	**12.5**	**9.0**
Freezing Point ^oF	**61**	**32**	**32**
Weight Equivalency	**1.37**	**1.27**	**1.0**

$2NaOH \Leftrightarrow 2Na^{+} + 2OH^{-}$ 2(40)g/mol ⇔ 2(23)g/mol + 2(17)g/mol **Typical Dosage: 68.5 mg/L** **100% Solubility ➔ High pH triggers carbonate formation and bacterial kills**	
$Ca(OH)_2 \Leftrightarrow CaOH^{+} + OH^{-} \Leftrightarrow Ca^{+2} + 2OH^{-}$ (74)g/mol ⇔ (57)g/mol + (17)g/mol ⇔ (40)g/mol + 2(17)g/mol **Typical Dosage: 63.5 mg/L** **100% Solubility ➔ High pH triggers carbonate formation and bacterial kills**	
$Mg(OH)_2 \Leftrightarrow MgOH^{+} + OH^{-} \Leftrightarrow Mg^{+2} + 2OH^{-}$ (58)g/mol ⇔ (41)g/mol (17)g/mol ⇔ (23)g/mol + 2(17)g/mol **Typical Dosage: 50 mg/L** **18% Solubility ➔ Moderate pH favors bicarbonate formation and bio-stability**	

"In the collection system, the magnesium hydroxide species I and II are favored over III, which helps to buffer pH between 8.0 and 9.0. Magnesium hydroxide works in H_2S reduction by a) neutralizing the first hydrogen ion in the H_2S molecule, b) shifting the pH to scavenge free H+ and favor the HS^- species, c) shifting away from a favorable pH range for SRBs and d) forming polysulfide compounds that prevent downstream flare-off during mixing with side streams.

"Magnesium hydroxide works in FOG reduction by a) slowly dissolving FOG accumulations at the FOG/water interface, and b) facilitating the biological reduction of FOG. Magnesium hydroxide makes FOGs more digestible by chemically breaking the large complex FOG compounds into simpler organic compounds. Furthermore, magnesium hydroxide enhances O_2 and CO_2 gas transfer at the air/water interface by breaking down the FOG blankets that can arrest biological digestion at the FOG/water interface."

The manufacturer of magnesium hydroxide also claimed that it would improve the settleability of the sludge in the final clarifiers by bonding at the molecular level. According to Premier Chemical's documentation settling floc in a nitrification system has negatively charged biopolymers from proteins in the polysaccharides that tend to repulse each other. Adding cations to wastewater changes the structure of the floc and the sludge dewaterability. Monovalent cations, such as sodium, form weak bonds between the negatively charged biopolymers and tend to decrease the density of activated sludge floc. Conversely, divalent cations, such as magnesium or calcium, participate in bridging of negatively charged sites on the biopolymers. The result is stronger bonds that cause the floc particles that form to be denser, larger, and more shear resistant. The effect of having a larger, more dense floc is an activated sludge with better settling ability. The ratio of monovalent to divalent cations is an indicator of how well floc will settle, with lower ratios leading to better setting. Dense floc also causes the resulting waste activated sludge to have better dewatering properties because less water is trapped between particles. Conversely, the magnesium typically binds with sulfates to form magnesium salts and discharges with the plant effluent. Therefore, $Mg(OH)_2$ does not increase the sludge production significantly.

Magnesium hydroxide has also been used successfully to control odor in collection systems. The main mechanism for odor control is pH adjustment. Magnesium hydroxide is added to the wastewater in order to increase the pH level above the range where sulfide production occurs, thereby limiting the amount of H_2S produced. It has been used as either an additive to the wastewater stream or been sprayed onto the surface of pipelines as a temporary coating.

Control of odor and corrosion in a collection system with magnesium hydroxide is a proprietary process. Premier Chemicals is the only manufacturer of magnesium hydroxide for odor and corrosion control. Premier Chemicals provides magnesium hydroxide slurry marketed under the product name Thioguard©. Several chemical suppliers can provide Thioguard©. The patent does not extend to the treatment process within the wastewater treatment plant, and a second manufacturer, Martin-Marietta, can produce magnesium hydroxide to supplement the nitrification process at a treatment plant.

ODOR CONTROL TEST METHOD

To perform the odor control test, magnesium hydroxide was introduced into the Kirkwood Lift Station wet well. The equipment included a 5,000 gallon bulk storage tank with a continuously operating mixer to keep the magnesium hydroxide from setting, a feed pump and discharge piping to the wet well.

The magnesium hydroxide slurry provided was 63 percent solids and was initially feed at a rate of 50 gallons per day. The magnesium hydroxide slurry weighs 13.2 pounds per gallon, and the weight of the magnesium hydroxide solids is approximately 8.0 pounds per gallon. On a daily basis, 400 pounds of magnesium hydroxide was feed into the lift station. The flow at the meter station was measured at an average of 771,000 gallon per day. Therefore, the concentration of magnesium hydroxide was 62.2 mg/L.

The test was run at 70 gallons per day and then at 50 gallons per day for the first tank load of magnesium hydroxide. The amount was turned down to 40 gallons per day, but there were odor complaints, so the feed was reset to 50 gallons per day.

An OdoLog was installed in the meter station vault to measure the H_2S concentration. The measurements were recorded weekly.

AIR PHASE ODOR CONTROL

Air-phase treatment of odors at the meter station was recommended by Alan Plummer Associates, Inc. (APAI) as a backup odor control system and to reduce the amount of magnesium hydroxide feed required. The meter station is located next to backyards of houses and a road, so space was not available for a biofilter and chemical scrubbers were not recommended. Two air-phase odor control options were identified: bioscrubbers and hydroxyl ion fog injection as manufactured by Vapex. TRA is familiar with bioscrubbers and their performance, but were unfamiliar with hydroxyl ion fog injection.

As described by the manufacturer, the Vapex® unit is potentially less obtrusive with less operation and maintenance costs than bioscrubbers. The Vapex unit produces a mist of OH^- radicals from ozone generated by using water, air, and electricity. The Vapex unit would be a quieter operation since it does not have a foul air fan, which would be needed with a bioscrubber. Because the Vapex© system uses no chemicals, the primary expenditures are upfront capital costs for the unit and power costs. The turnkey cost for the unit employed during this study is $60,000 with annual operating costs ranging from $1,200-$2,300 depending on the kilowatt per hour rates.

Another advantage of the Vapex unit is that it does not create a negative pressure on the collection system, which the supply fan for bioscrubbers would do. The negative pressure would cause more H_2S to come out of solution than would otherwise occur, which means there is more H_2S load on the bioscrubber.

TRA decided to pilot test a Vapex® unit at the KirkwoodMeter Station in conjunction with the chemical feed in lieu of using a bioscrubber. Figure 1 shows the relative locations of the Kirkwood Lift Station and Meter Station where data measurements were taken.

The Vapex odor control system was installed at the meter station with an application point at the meter station and at the first manhole downstream of the meter station. The downstream manhole is a drop manhole that is a major release point for the H_2S and is also the sewer connection to a small municipality. The turbulence caused by the drop and by the introduction of additional flow strips a large portion of the remaining H_2S out of the wastewater.

TRA personnel connected potable water and 120 V power to the Vapex unit. The OH^- radicals were dispersed in the meter vault and the downstream drop manhole using a nozzle that creates a vapor mist from the ozone and water. The mist fills the head space and reacts with the sulfide particles.

Denton Creek Regional Wastewater System

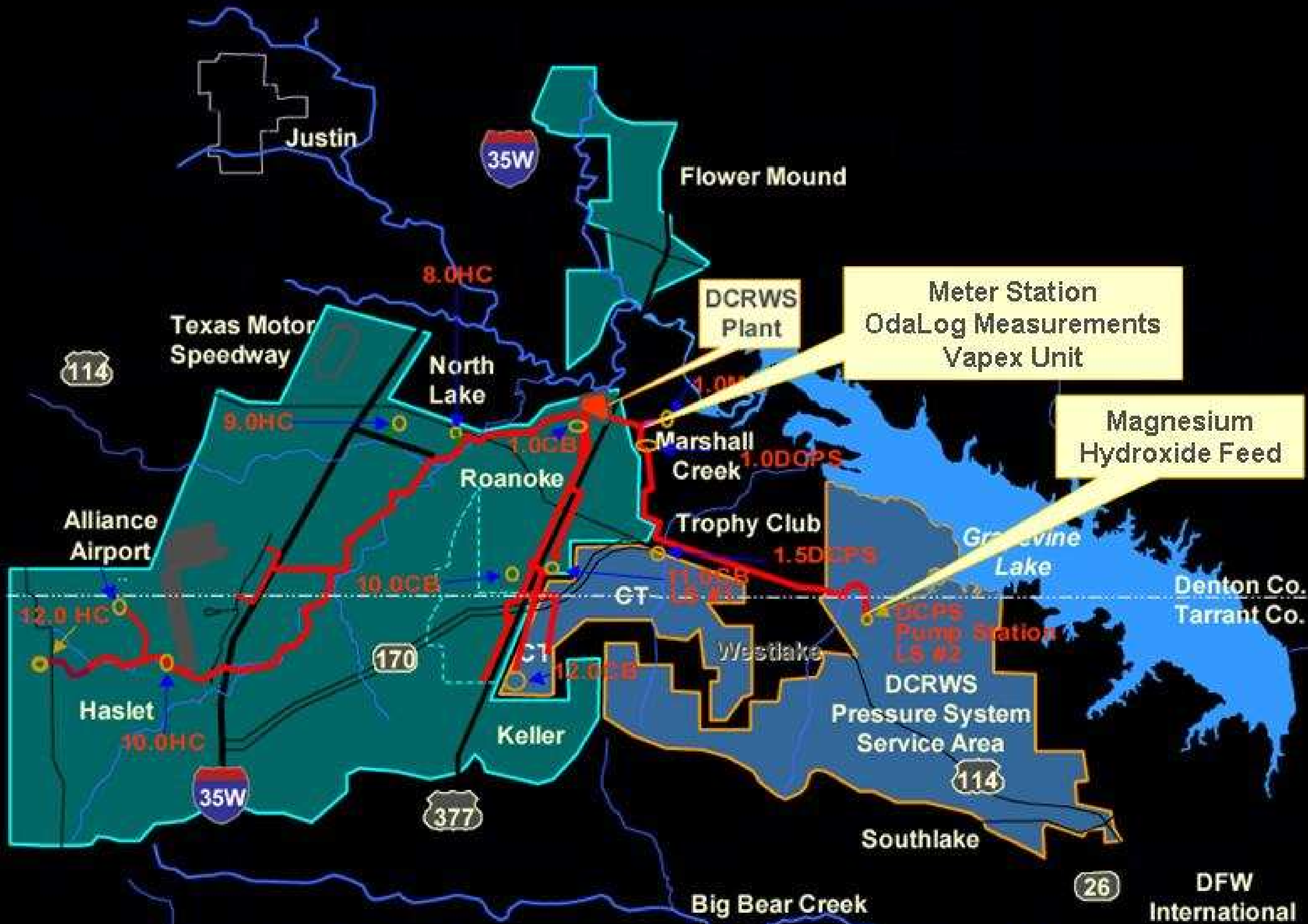

Figure 1: Relative Locations of the Magnesium Hydroxide Feed, Vapex Unit, and OdaLog

RESULTS

Magnesium Hydroxide© Feed at Kirkwood Pump Station and Southlake Metering Station

Baseline data was taken prior to the implementation of the magnesium hydroxide feed and is shown in Figure 2. H_2S measurements were taken at the Southlake Meter Station, just prior to the Denton Creek RWS influent.

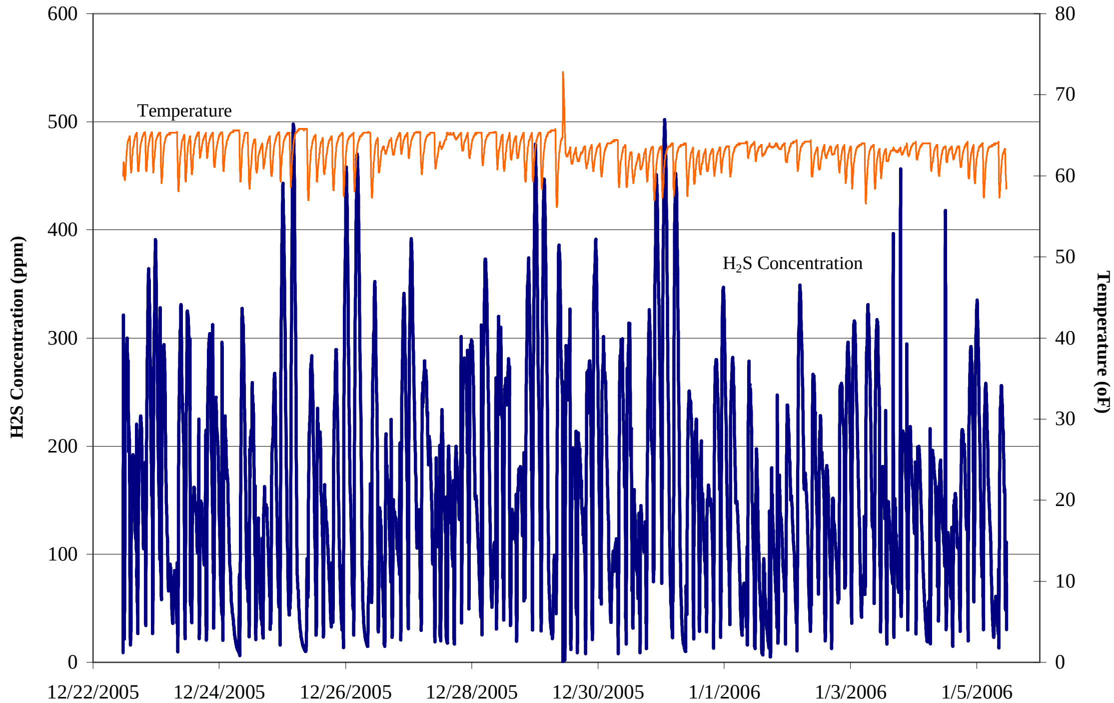

Figure 2: Baseline Hydrogen Sulfide Concentration at the Southlake Metering Station

The average concentration of H_2S was 166 ppm, and it peaked between 400-500 ppm. Based on the prior examination of the Kirkwood Pumping Station by APAI, these peaks were correlated to pump cycling.

The magnesium hydroxide feed pumping rate was initially matched to the pump station pumping cycles, and testing began on January 31, 2006. Metering problems prevented proper dosing until February 2. As shown in Figure 3, at the beginning of the test, there are peak concentrations similar to those evidenced in the baseline data. It was determined that these peaks were occurring because the magnesium hydroxide feed pump was not operating every time the lift station pumps ran. The magnesium hydroxide feed arrangement was modified to feed directly into the pump station wet well continuously at a feed rate of 70 gallons per day.

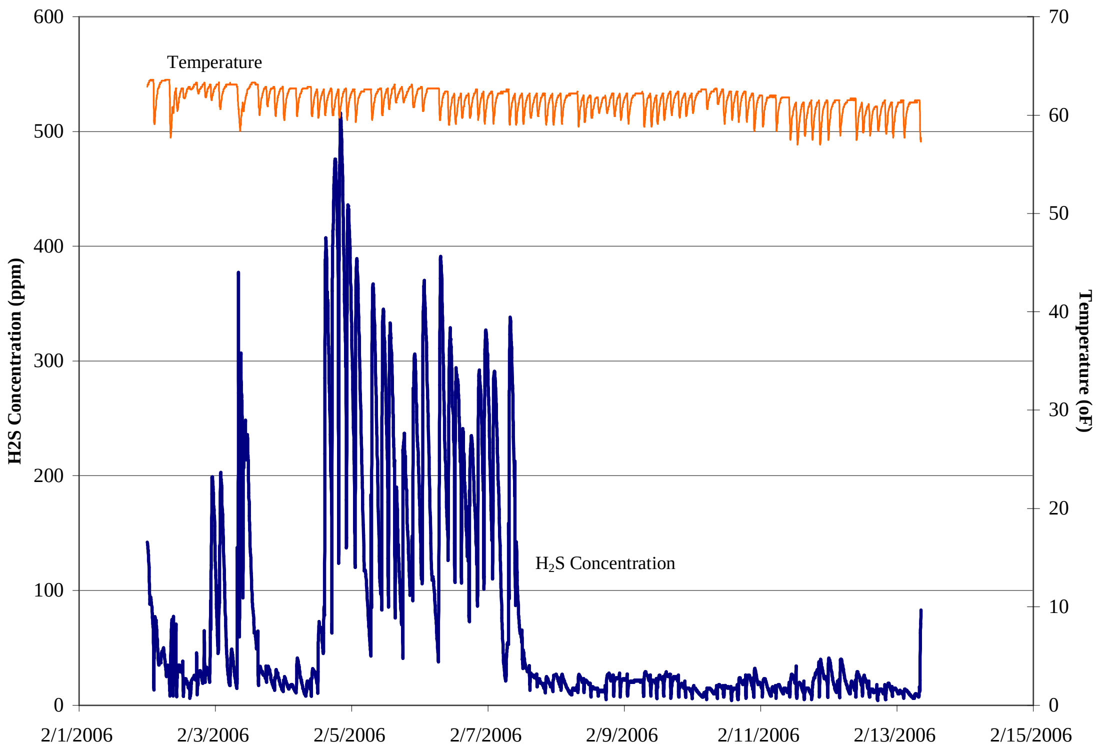

Figure 3: Hydrogen Sulfide Concentrations After Dosing with Magnesium Hydroxide

Following this feed modification, these concentrations soon dropped dramatically, indicating that the magnesium hydroxide was producing a significant reduction in H_2S concentration.

Further studies were conducted in the warmer spring and summer months, resulting in approximately the same levels of H_2S removal. Some data was also taken at the Kirkwood Pump Station at the site of the feed. The average H_2S concentration was approximately 10 ppm, which, in spite of having limited baseline data, demonstrates the magnesium hydroxide's ability to maintain safe and aesthetically acceptable levels of odor causing compounds.

Vapex® Unit Within the Metering Station

Vapex® uses a specialized nozzle to form a hydroxyl ion fog from water and ozone; the fog collects odorous compounds and returns them to the water stream without the compounds being vented to atmosphere. A Vapex® unit was installed in the Southlake Metering Station and run in conjunction with the magnesium hydroxide feed. Figure 4 demonstrates the H_2S concentrations in the meter station prior to and during the unit's operation.

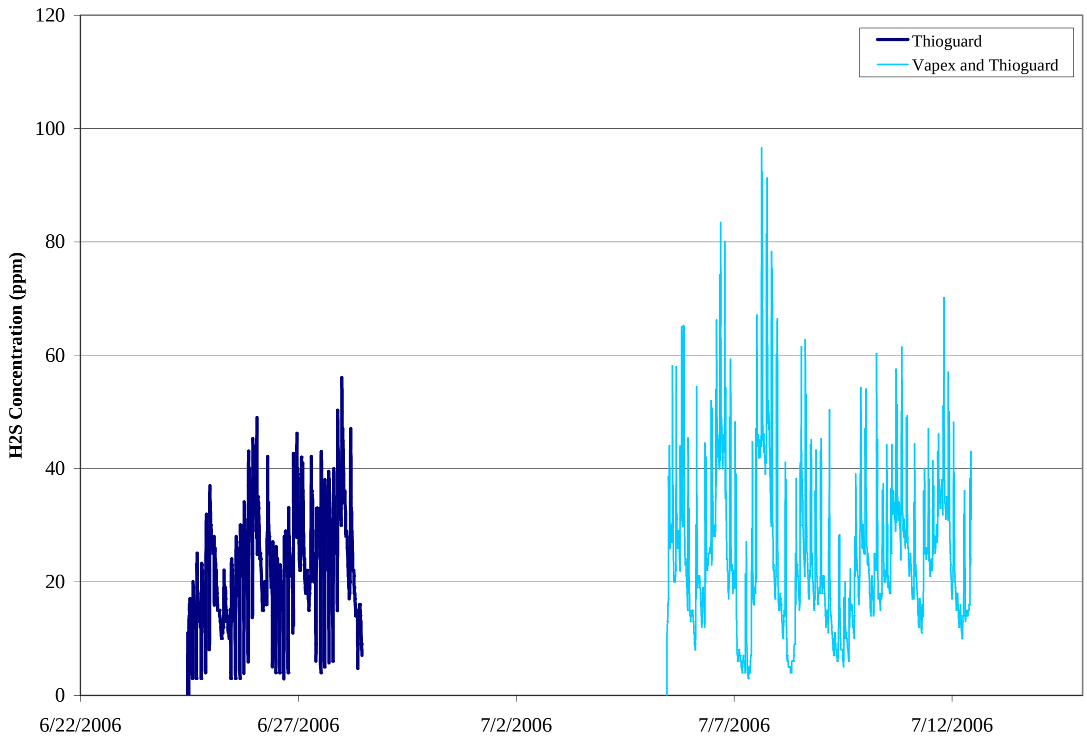

Figure 4: Apparent increase in H_2S due to hydroxyl ion fog in reactor. Possible erroneous measurement of H_2S by OdaLog

The average concentration of H_2S is higher and the peaks are greater when the Vapex unit is running. This result was contradictory to what was expected. Since the concentration of magnesium hydroxide was not changed, it appears that the hydroxyl ion fog was causing more H_2S to come out of solution. The Vapex manufacturer said that the hydroxyl ion fog would cause the measuring device to misread the amount of H_2S. The OdaLog representative disagreed with this position and said that there should be no effect.

As a means of resolving this conflict from an overall point of view, the DCRWS staff turned off the magnesium feed starting July 12 and operated for a month in the summertime conditions with only the Vapex® unit running. During this time period the plant received no odor complaints. As a comparison, in March, the magnesium feed stopped for two days before the feed was restarted, and the plant received odor complaints at the meter station during those two days. Therefore, outside the meter station reactor, the Vapex® unit successfully eliminated odor complaints during the hottest time of the year.

ALKALINITY TEST AT TREATMENT PLANT

The DCRWS wastewater treatment plant has two identical secondary treatment units (STU), each with two aeration basins, two rectangular final clarifiers and separate return activated sludge pumps. Each STU has a design capacity of 1.1 MGD. A magnesium hydroxide slurry feed station was set up at the secondary treatment flow division box. Magnesium hydroxide was fed to the STU-1 only at a rate of approximately 80-90 gallons per day. The plant staff recorded influent and effluent pH, discharge BOD, TSS and NH3-N from each train. The timing of the testing was arranged to coincide with the November 2005 NASCAR race event.

The DCRWS treatment system does not have primary clarifiers, so the aeration basins normally have a higher mixed liquor concentration due to the additional non-organic solids. In preparation for the race event, the plant staff allowed the solids load in the basins to increase. Also, issues with the sludge dewatering system caused the mixed liquor solids concentration to increase during the test. During the test, the solids load was very high, and pin flocking appeared, so the test was only performed for six weeks. The results of the test are shown in Table 1. The pH in STU-1 was higher than in STU-2 over the course of the test. However, both units obtained full nitrification, so the test was unable to determine improvement in the nitrification process. There was not a significant difference in sludge settleability, although a brief discussion is warranted:

The sludge volume index (SVI) is a measure of solids settleability, calculated by dividing the volume a sludge sample settles during a prescribed period of time by the MLSS concentration. SVIs are ideally kept below 100. Table 1 shows the average SVI for each aeration basin; each treatment train is comprised of two basins and therefore the appropriate aeration basin SVIs were averaged to establish an overall SVI for the treatment train. There is a 17 percent difference between the SVI of the STU-1 and STU-2, which would seem to indicate that the $Mg(OH)_2$ was in fact improving, however marginally, the SVI. However, the MLSS concentrations of STU-1 were much higher than those in STU-2, which would certainly contribute to lower SVIs in the former, driven by a process characteristic unrelated to the magnesium hydroxide feed. Therefore, at the very least, the data are inconclusive regarding the SVI relative to magnesium hydroxide dosing, and it is highly possible that there was no effect.

Table 1: Comparison of Operational Parameters With and Without $Mg(OH)_2$ Feed

	STU-1 **With $Mg(OH)_2$ Feed**	STU-2 **Without $Mg(OH)_2$ Feed**
SVI	50.1	58.6
MLSS Concentration	7102	5502
Effluent pH	7	7
Effluent Alkalinity	261	147

Despite the lack of improvement in settleability, there were benefits to the alkalinity and pH stabilization. Keeping the pH of a biological treatment system stable and between the ideal range, therefore, is critical. Table 1 demonstrates that the treatment units fed with magnesium hydroxide remained closer to the appropriate pH range, while the other aeration basins neared the point at which nitrification is affected. Coupled with the pH buffering is the alkalinity that the magnesium hydroxide provides. It is recommended that an alkalinity of 150 mg/L be maintained after nitrification, and that this measurement be taken before secondary sedimentation. Table 1 also shows the alkalinity of the aeration basin effluent for the treatment trains with and without the magnesium hydroxide feed. The alkalinity remaining in the aeration basin effluent was much higher in STU-1 than in STU-2

MAGNESIUM HYDROXIDE COSTS

The raw cost of the magnesium hydroxide feed is approximately $2.05 per gallon, and an effective odor removal feed of approximately 50 gallons per day was employed in this pilot study at the Kirkwood pump station without the Vapex unit on-line. At this feed rate, the cost of the magnesium hydroxide is approximately $37,400/year. With the Vapex unit operating, the magnesium hydroxide feed was reduced to 33 gallons per day, which equates to a cost of approximately $24,700/year. Also, it is anticipated that the magnesium hydroxide would be fed at the plant during race events and the associated high ammonia loads to buffer the alkalinity and maintain the pH level.

CONCLUSIONS

The following conclusions were made from the tests

- Magnesium hydroxide reduced the level of hydrogen sulfide substantially and proved to be a benefit to the plant by stabilizing the pH within the biological treatment units and providing additional pH buffer in the form of alkalinity.
- The magnesium hydroxide did not noticeably improve the settleability of the mixed liquor solids during the test; however, the high amount of solids in the test basins may have caused the pin floc to form despite the presence of magnesium hydroxide.
- The hydroxyl ion fog producing Vapex© unit eliminated odor complaints when it operated without magnesium hydroxide.

ACKNOWLEDGEMENTS

We appreciate the assistance of Matthew Madolora, with Premier Chemicals, during the testing phase and with information on magnesium hydroxide.