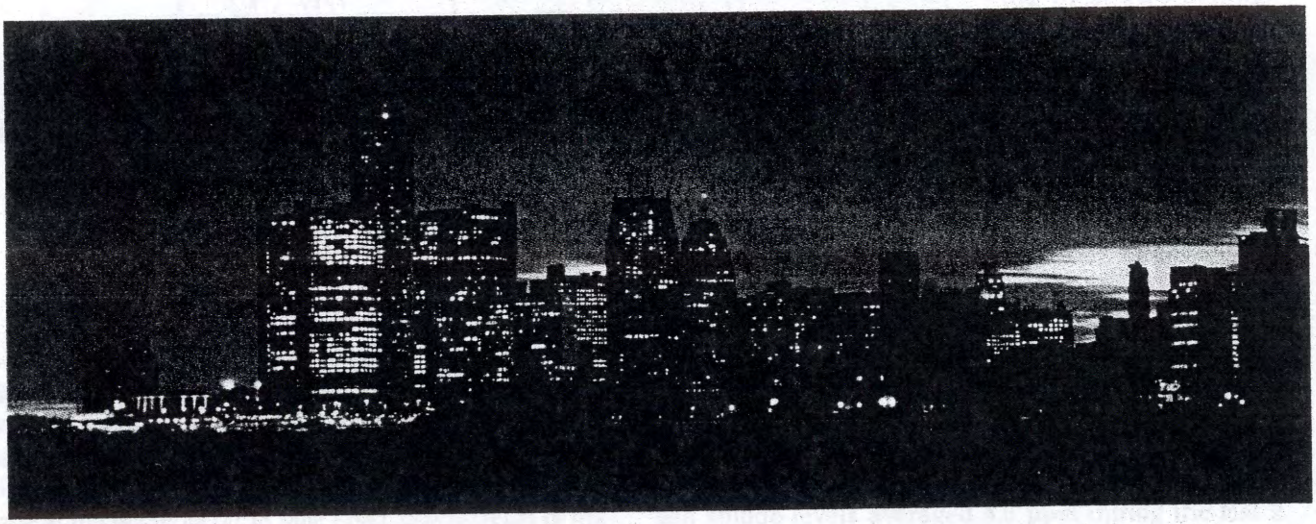
The Benefits of Calcium



Chemical addition cuts odors in a Michigan collection system interceptor

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When real estate developments near a pump station and interceptor on Garfield Road led to larger wastewater volumes and more frequent odor complaints from adjacent residents and businesses, the Detroit (Mich.) Water and Sewerage Department (DWSD) found that calcium nitrate injection solved the problem.

Odor Problem

The 4.8-km-long (3-mi-long) section of the Romeo Arm Interceptor along Garfield Road between 18 and 21 Mile Roads is a 600-mm (24-in.) prestressed concrete force main. It transports wastewater from a pump station at 21 Mile and Garfield Roads that collects wastewater from Shelby, Macomb, and Clinton, Mich. Wastewater from Sterling Heights and Clinton discharges to the 2700-mm-diameter (108-in.-diameter) interceptor through two additional connections at 18 Mile Road and Clinton River Road.

Because the force main always flows full, bacteria in the wastewater lack oxygen and so anaerobically decompose sulfur compounds during the long detention time, producing sulfides. When the force main discharges to the gravity interceptor through a drop manhole at 18 Mile Road, the resulting turbulence releases considerable amounts of hydrogen sulfide into the atmosphere.

Hydrogen sulfide is the most commonly known and prevalent odorous gas associated with domestic wastewater collection and treatment systems. It has a "rotten egg" odor, is extremely toxic, corrodes some metals, and is a precursor to the formation of sulfuric acid, which corrodes such materials as concrete.

Chemicals Preferred

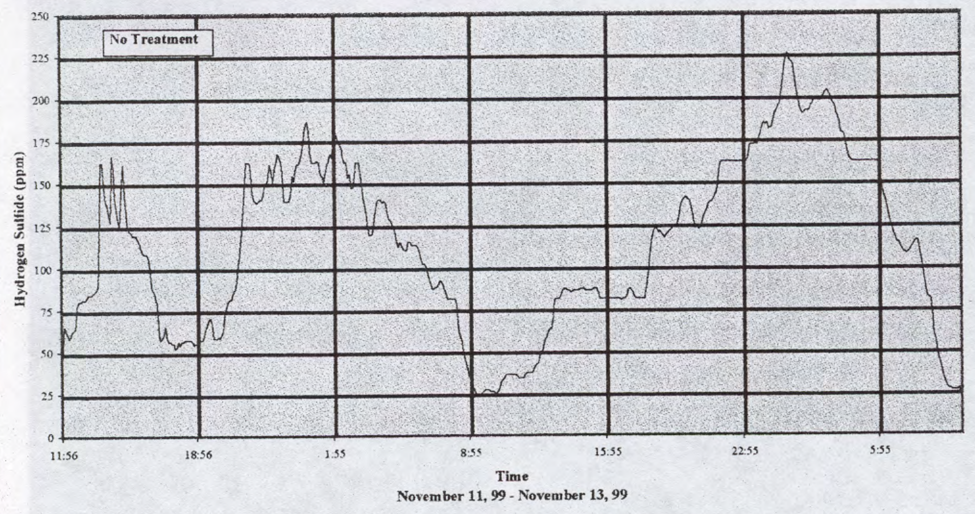
DWSD hired a consultant to solve the odor problem. After reviewing various available odor control technologies, the project team determined that a liquid-phase treatment system would be the most appropriate method for the Romeo Arm Interceptor. Such systems inject a biological oxygen source or pH modifier into a force main to control the production and release of hydrogen sulfide gas.

Calcium nitrate provides a source of biological oxygen to bacteria for respiration that prevents the production of and helps remove hydrogen sulfide. Magnesium hydroxide is a commonly used pH modifier that raises wastewater pH to approximately 8.5 to keep hydrogen sulfide in liquid phase.

The team invited magnesium hydroxide and calcium nitrate suppliers to present information and distribute literature about their products at DWSD's Water Board Building on June 22 and July 7. The suppliers then were invited to conduct a preliminary investigation of wastewater quality in the interceptor and submit proposals by Aug. 3. After evaluating these proposals, the project team recommended the calcium nitrate option (see table, p. 47).

The team conducted a full-scale pilot test from Nov. 11 to Dec. 17, 1999. Wastewater was treated by injecting calcium nitrate into the water in the interceptor manhole

Figure 1. Baseline Concentrations of Hydrogen Sulfide in the Romeo Arm Interceptor



upstream of the Garfield pump station. This manhole is at the intersection of 18 Mile Road and Garfield Road, where the force main discharges to the interceptor. Chemical injection began at 5:00 p.m. on Nov. 13. Measurements were made at the manhole on 18 Mile Road, downstream of the one where the injection equipment was installed.

The pump station's design capacity is 0.57 m^3/s (20.0 ft^3/s), but the maximum day or instantaneous peak flow recorded is 0.51 m^3/s (18.10 ft^3/s). Daily flows during testing ranged from 0.22 to 0.30 m^3/s (7.93 to 10.44 ft^3/s) and averaged 0.26 m^3/s (9.34 ft^3/s).

Team members used the flow data to determine the initial chemical dose and then adjusted it, as needed, to arrive at the optimum treatment level. Calcium nitrate doses ranged from 0.49 to 0.6 m^3/d (130 to 159 gal/d) and averaged 0.54 m^3/d (143 gal/d).

Pilot Test Results

Atmospheric hydrogen sulfide. *Baseline (no treatment).* The team monitored baseline atmospheric hydrogen sulfide concentrations continuously from 8:01 a.m. on July 11 to 6:35 a.m. on July 14 and from 11:56 a.m. on Nov. 11 to 10:05 a.m. on Nov. 13. In July, hydrogen sulfide concentrations ranged from 21.0 to 306.0 ppm and averaged 143.5 ppm; in November, levels ranged from 23.0 to 226.0 ppm and averaged 113.0 ppm (see Figure 1, above).

Team members also used hydrogen sulfide detector tubes during the demonstration period to selectively verify results obtained by STX 70 during continuous monitoring. Detector tubes were used only on days when field testing was conducted. Results obtained with both methods were nearly identical.

Treatment with calcium nitrate. During demonstration testing from Nov. 15 to Dec. 17, atmospheric hydrogen sulfide concentrations ranged from zero to 194.0 ppm and averaged 9.6 ppm (see Figure 2, p. 48).

Project team members noticed that atmospheric hydrogen sulfide levels were high from 12:47 p.m. on Nov. 21 to 06:02 a.m. on Nov. 22 and from 11:15 a.m. on Nov. 25 to 11:25 a.m. on Nov. 26, indicating that practically no treatment occurred during these two periods. Discussions with DWSD personnel revealed that maintenance crews had been onsite then, which led the team to believe that the chemical feed pumps' power supply might have been switched off inadvertently on those days.

When results from these two periods were ignored, hydrogen sulfide concentrations ranged from zero to 60 ppm and averaged 6.1 ppm. The system seemed to stabilize about 3 weeks after chemical injection began, and atmospheric hydrogen sulfide levels averaged 4.6 ppm during the last 2 weeks of testing.

Typically, a concentration of 0.5 ppm may cause a strong odor, but a concentration of less than 10 ppm is not an immediate health hazard. So, the average hydrogen sulfide concentration measured during testing (about 5 ppm) is a safe level of control, compared to the untreated average concentration of 113 ppm or untreated maximum of 226 ppm, which could cause eye and respiratory injury in humans.

Total dissolved sulfide. Before chemical injection began, total dissolved sulfide concentrations ranged from 0.2 to 1.1 mg/L. During demonstration testing, total dissolved sulfide levels dropped to zero.

Calcium nitrate performance. Calcium nitrate injection treatment had an overall removal efficiency of 91.5% without any adjustment to recorded data. This analysis included all data recorded during demonstration testing.

When the two extreme hydrogen sulfide concentration periods were removed from consideration, the injection system's overall removal efficiency was 94.6%. The system stabilized after 3 weeks of treatment, and removal efficiency for the last 2 weeks was 95.9%.

pH. Before chemical injection began, wastewater pH ranged from 7.0 to 7.9. During the demonstration period, wastewater pH ranged from 1.7 to 7.7.

The 1.7 pH measurement occurred at 11:30 a.m. on Nov. 16, when the wastewater was "milky" colored. When the team checked pH again 10 minutes later, the wastewater still was milky, but pH had increased to 5.7. By 12:40 p.m., the pH had returned to normal. The incident never recurred.

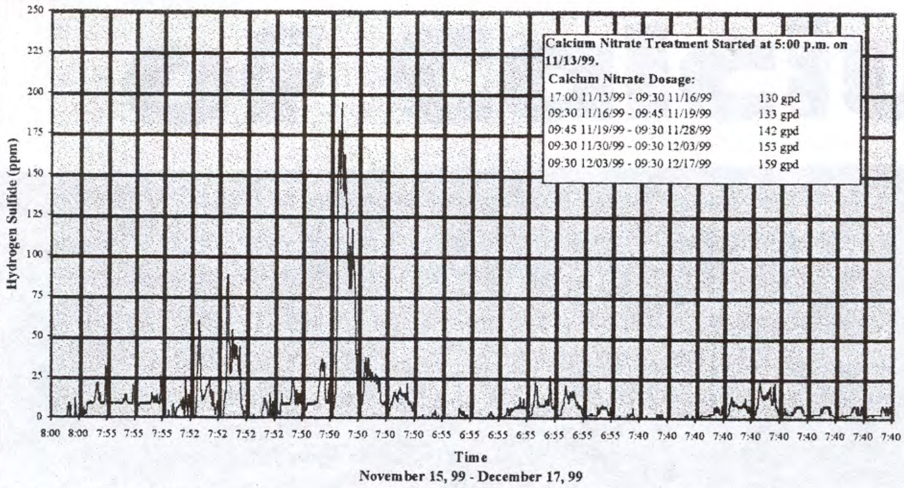
Temperature. Overall, wastewater temperature was fairly constant. A few days before chemical injection began, the average ambient temperature ranged from 6°C to 17°C (43°F

Comparison of Magnesium Hydroxide and Calcium Nitrate for Odor Control

Magnesium hydroxide	Calcium nitrate	Remarks
1 Chemical Reaction		
Magnesium hydroxide is a pH modifier and raises the pH of wastewater to approximately 8.5, which suppresses the release of hydrogen sulfide gas; however, does not reduce the production of or remove any sulfides.	Calcium nitrate provides a source of biological oxygen to the facultative bacteria (sulfate reducing) that bio-oxidizes the pre-existing sulfides and prevents the formation of hydrogen sulfide.	Magnesium hydroxide and calcium nitrate react quite differently from each other to control an odor problem. Magnesium hydroxide may be better in one situation while calcium nitrate may be in others.
2 Physical properties		
Magnesium hydroxide requires continuous mixing and material can dry/cake on tank walls or during transport. Slurry is more abrasive to pump than calcium nitrate. More power is required to pump slurry due to higher viscosity. Freezes at a temperature of 32° F.	Calcium nitrate does not require continuous mixing. Solution is not abrasive. Less power is required to pump solution due to lower viscosity. Does not freeze.	Magnesium hydroxide requires additional equipment to continuously mix the slurry. Pumps require higher power to pump slurry to the application point.Only the pumps made of abrasion resistance material can be used. The freezing point of magnesium hydroxide is 32° F that is commonly achieved during winter in Michigan.This will require additional care not to let it freeze. For magnesium hydroxide, continuous flushing of pipe lines, tanks and other equipment is required. Magnesium hydroxide requires higher maintenance cost.
3 Cost to DWSD		
The cost of a 60-day trial for using magnesium hydroxide would be $159,888.	The cost of using calcium nitrate for a 30-day trial demonstration would be the cost of chemical only ($7000), if a guaranteed performance of 85% control of atmospheric hydrogen sulfide and less than 0.5 ppm of dissolved sulfide is achieved. If this level is not achieved then there would be no cost.	
4 Safety and health concerns		
Magnesium hydroxide is a GRAS (generally regarded as safe) substance.	Calcium nitrate contains no hazardous substance (as listed in 40 *CFR* 302). Hazardous decomposition products are nitrogen oxide and ammonia.	There has been no complaint of any health hazard associated with the use of calcium nitrate in over 400-600 installations nationwide. However, it was recommended to investigate the production of nitrogen oxide compounds, if DWSD decides to use calcium nitrate.
5 DWSD to supply		
• Fresh water hose bib to flush discharge lines and clean up. • Concrete pad 12 ft x 24 ft. • Boom truck or fork lift. • Multi channel loop-powered isolator. • A three-phase 460 VAC power supply. • DWSD personnel to meet delivery truck daily. • Unlimited access to the pumping station. • Requires the construction of an insulated building for permanent installation.	• Fresh water supply is optional. • Concrete pad or gravel pad of 12 ft diameter is sufficient. • 115 V power supply. • Truck access for filling the storage tank. • DWSD personnel to meet delivery truck approximately once a month. • Doesn't require a building to house the unit even during winter.	The items to be supplied by DWSD for use of calcium nitrate requires less manpower, equipment, building space, and water and power supply.
6 Previous installations in Michigan		
None.	Seventeen customers with 26 installations.	Calcium nitrate is being used at different locations under Michigan conditions. It was expected that calcium nitrate performance could be repeated under similar meteorological conditions.

For independent references on the efficacy of using magnesium hydroxide and calcium nitrate for odor control, the project team contacted Jim Joyce, technical director at Odor and Corrosion Technology Consultants Inc. (Houston, Texas); Bill Francis, assistant director of water and wastewater at the City of Brunswick, Ga.; Robert Webb and Ron Maze in the Water Service Department at Phoenix, Ariz.; Tom Rook at the Gun Lake (Mich.) Area Sewer Authority; and Scott Vanleum at the Battle Creek (Mich.) Wastewater Treatment Plant.

Figure 2. Effects of Calcium Nitrate on Hydrogen Sulfide Concentrations in the Romeo Arm Interceptor



to 62°F), and the baseline wastewater temperature ranged from 15.6°C to 18.3°C (60.2°F to 64.9°F). During the demonstration period, the average ambient temperature ranged from 3°C to 14°C (37°F to 57°F), and the baseline wastewater temperature ranged from 14.4°C to 17.7°C (58.0°F to 63.9°F). Therefore, the team determined that the calcium nitrate dosage could remain at about this level during winter, but probably would need to be increased during summer to compensate for expected wastewater temperature increases.

Residual nitrate. Residual nitrate concentrations were virtually constant — only ranging from 0.1 to 0.5 mg/L — indicating that chemical treatment dosages were optimal during the demonstration period.

Nitrogen oxide compounds. The team used detector tubes to measure nitrogen dioxide, total nitrogen oxides, nitric oxide, and nitroparaffin. Nitrogen dioxide, total nitrogen oxide, and nitric oxide concentrations were below detection limits, while nitroparaffin levels were either less than the detection limit or less than 0.5 ppm for all samples tested under baseline conditions.

Once calcium nitrate injection began, nitrogen dioxide, total nitrogen oxide, and nitric oxide concentrations remained below detection limits. Nitroparaffin concentrations ranged from non-detect to 3.5 mg/L, suggesting that trace levels of nitrous oxide might have been present. However, because no positive values were seen for the other nitrogen oxide compounds, the nitroparaffin measurements could be due to another "nitro-organic," such as nitromethane, nitroethane, nitropropanes, and acetonitrile. (The nitroparaffin detector tube has been reported to detect the presence of such compounds.)

Additional Benefits

Overall, the project team concluded that calcium nitrate injection would control interceptor odors cost-effectively. The cost of chemical feed and storage equipment with a 24-m^3 (6400-gal) double walled tank installed would be about $50 000. The cost of the chemical would be about $7000 per month.

It also would control corrosion in the 2.7-m-diameter (9-ft-diameter) concrete gravity sewer and eliminate the possibility of subsequent hydrogen sulfide releases downstream of 18 Mile Road.

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