The Benefits of Calcium

Chemical addition cuts odors in a Michigan collection system interceptor
Kathleen Leavey, James Heath, Jay Shah, Bharat Doshi, S.P. Singh, Ted Znoy, and Dave Lakin

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
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 injec-
tion 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 treat-
ment). The team monitored baseline atmospheric hydro-
gen 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
centresations ranged from 21.0 to 306.0 ppm and aver-
age 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
these two periods were ignored, hydrogen sulfide con-
centrations 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 hydro-
gen 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 hydro-
gen 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 max-
imum 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 injec-
tion 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 sys-
tem stabilized after 3 weeks of treatment, and removal effi-
ciency 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 fair-
ly 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

<table>
<thead>
<tr>
<th>Magnesium hydroxide</th>
<th>Calcium nitrate</th>
<th>Remarks</th>
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<tbody>
<tr>
<td><strong>1. Chemical Reaction</strong></td>
<td>Calcium nitrate provides a source of biological oxygen to the facultative bacteria (sulfate-reducing) that biooxidizes the pre-existing sulfides and prevents the formation of hydrogen sulfide.</td>
<td>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.</td>
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<td>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, it does not reduce the production of or remove any sulfides.</td>
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<td><strong>2. Physical properties</strong></td>
<td>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.</td>
<td>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-resistant 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.</td>
</tr>
<tr>
<td>Magnesium hydroxide requires continuous mixing and material can dry, make 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.</td>
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<tr>
<td><strong>3. Cost to DWSN</strong></td>
<td>The cost of using calcium nitrate for a 30-day trial demonstration would be the cost of chemical only ($7,000). It is 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.</td>
<td>There has been no complaint of any health hazard associated with the use of calcium nitrate in over 400,000 installations nationwide. However, it was recommended to investigate the production of nitrogen oxide compounds. If DWSN decides to use calcium nitrate.</td>
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<td>The cost of using magnesium hydroxide for a 30-day trial demonstration would be the cost of chemical only ($7,000). It is 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.</td>
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<td><strong>4. Safety and health concerns</strong></td>
<td>Calcium nitrate contains no hazardous substances (as listed in 40 CFR 302). Hazardous decomposition products are nitrogen oxide and ammonia.</td>
<td>The items to be supplied by DWSN for use of calcium nitrate includes manpower, equipment, building space, and water and power supply.</td>
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<td>Magnesium hydroxide is a GRAS (generally regarded as safe) substance.</td>
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<td><strong>5. DWSN to supply</strong></td>
<td>Fresh water supply is optional.</td>
<td>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.</td>
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<tr>
<td>Be in water base to flush discharge lines; and clean up.</td>
<td>Concrete pad or gravel pad of 12 ft diameter is sufficient.</td>
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<td>Concrete pad 12 ft in dia.</td>
<td>115 V power supply.</td>
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<td>Boom truck or tank lift.</td>
<td>Truck access for filling the storage tank.</td>
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<td>Mud auger or low-powered auger.</td>
<td>DWSN personnel to meet delivery and operate mixing.</td>
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<tr>
<td>A three-phase 500 VAC power supply.</td>
<td>Unlimited access to the pumping action.</td>
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<td>DWSN personnel to meet delivery and operate mixing.</td>
<td>Requires the construction of an insulated building for permanent installation.</td>
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<td><strong>6. Previous installations in Michigan</strong></td>
<td>Seventeen customers with 26 installations.</td>
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<td>None.</td>
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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 at the Water Service Department at Phoenix, Ariz.; Tom Rock at the Gun Lake (Mich.) Area Sewer Authority; and Scott Vanleum at the Battle Creek (Mich.) Wastewater Treatment Plant.
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 nitroparaffins. 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 nondetect 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-m³ (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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