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Pickling a new natural gas pipeline

Northeast Gas Association
Gas Operations School
June, 3 2020
Wesley Lucas, Sales Director

Why do we odorize natural gas?

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New London, TX

- In the United States for all practical purposes odorization of natural gas originated due to the explosion of London school in the small east Texas town on New London on March 18, 1937.

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Approximately 600 students and 40 teachers were in the building at the time.

Approximately 300 students and teachers perished.

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Objectives of Odorization

- **SAFETY** of end-users and gas pipeline workers
- LEGAL REQUIREMENT:
  - In the U.S.: D.O.T.'s Office of Pipeline Safety enforces regulation 49 CFR 192.625(a), stating that "*natural gas must be odorized so that any leaks are readily detectable, by a person with a normal sense of smell, when the concentration of natural gas reaches 1/5th of the lower explosive limit.*"

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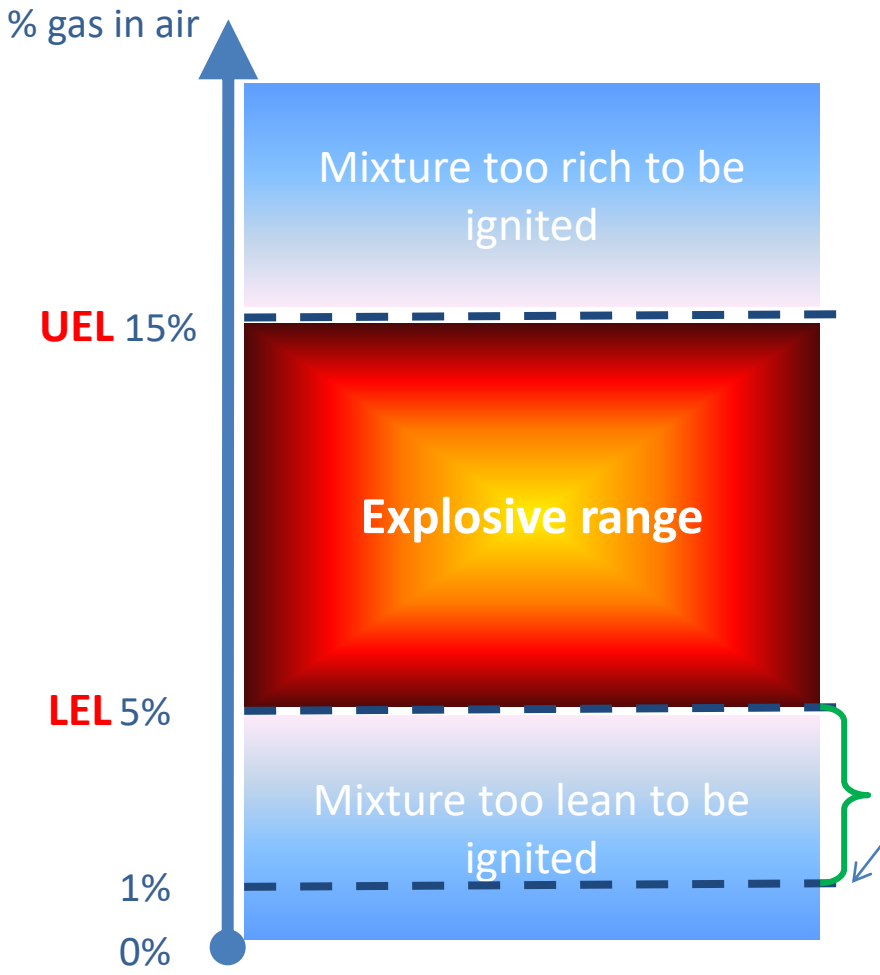
Why 1/5th of the L.E.L.?



Setting the detection requirement at 1/5th of the LEL, i.e. at 1% gas in air, builds in a **safety factor** and allows time to respond to a detected leak before the gas/air mixture is able to support ignition.

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The mere presence of odorant is not enough

- Ultimately, a person must be able to detect a gas leak.
- …which is why the human nose and yes/no perception are still the only valid assessment techniques. Primary device used Gas Dilution Apparatus (Odorometer, Odorator, DTEX)

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What is Odor Fade?

When a new natural gas steel pipe is installed, the porous inner wall of the pipe contains metal oxides (rust and mill scale) which will react with odorant, e.g. *tert*-butyl mercaptan (TBM), to produce disulfides. Disulfides have lower vapor pressures and are less odorous than TBM.

Therefore perfectly odorized gas entering the pipe will be stripped of odorant as it flows down the pipe and will be left odorless at the outlet.

Causes:

- Ferric oxides (rust) – from hydrotest, welding, pipeline storage
- Adsorption/absorption of mercaptan into porous metal or PE surface
- Odor masking from pipeline condensates, disulfides, background odor of natural gas

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GAS ODORANTS

ODOR-FADE WARNING

A GAS LEAK CAN CAUSE A FIRE OR EXPLOSION RESULTING IN SERIOUS INJURY OR DEATH.

Be aware that the stenching chemical added to gas to make it detectable may not warn of a gas leak or the presence of propane or natural gas to all persons in every instance. Instances where the odorant in an odorized gas may be undetectable include: • Odor intensity may fade or be eliminated for a variety of chemical and physical causes, including the oxidation of rusting pipes, adsorption into or sticking onto the interior of pipes or appliances, or absorption into liquids. • Contact with soil in underground leaks may de-odorize or remove odorant from the gas. • Some people have a diminished ability, or inability to smell the stench. Factors that negatively affect a person's sense of smell include age, gender, medical conditions, and alcohol/tobacco usage. • The stench of odorized gas may not awaken sleeping persons. • Other odors may mask or hide the stench. • Exposure to the odor for even a short period of time, may cause nasal fatigue, where a person can no longer smell the stench.

Gas detectors listed by the Underwriters Laboratories (UL) can be used as an extra measure of safety for detecting gas leaks, especially under conditions where the odorant alone may not provide an adequate warning. Gas detectors emit a loud, shrill sound when gas is present and do not depend on sense of smell. Because the odor intensity can fade or people may have problems with their sense of smell, we recommend installing, per manufacturer's instructions, one or more combustible gas detectors, in suitable locations to ensure adequate coverage to detect gas leaks. Educate yourself, your employees, and your customers with the content of this warning and other important facts associated with the so-called "odor-fade phenomenon".

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- SOURCE: HTTP://WWW.CPCHEM.COM/BL/SPECCHEM/EN-US/PAGES/ODOR-FADE-WARNING.ASPX

Why is Knowledge of Odor Fade Important?

1. It occurs in 100% of new steel, PE, internal epoxy coated lines.
2. If not accounted for, odor fade will put at risk the reliability of safe natural gas distribution.
3. Odor fade is difficult to recover from. Takes time, manpower and equipment.
4. If not detected, it puts our clients at risk for un-odorized gas
5. Good planning will save you time and manpower → avoid responding to odor fade with no easy way to recover.

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Chemistry of Odor Fade

Organic disulfides are produced by oxidation of mercaptans according to the general reaction:

2R--SH+Oxidant→R--S--S--R+Reductant

Oxidant = rust – ferric oxide
Ruductant = ferrous sulfide

Ferrous Sulfide will in essence coat the internal wall of the steel pipe and no longer react with mercaptan.
At this point, the pipeline will no longer exhibit odor fade.

Note: moisture (oxygen) input into pipeline can generate more oxides which will react with mercaptan to cause odor fade. This is mostly noticeable in already conditioned pipeline that has very low or no flow conditions.

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Consequences of Odor Fade?

Federal Regulation 49 CFR Part 192.625 states: *"A combustible gas in a distribution line must contain a natural odorant or be odorized so that a concentration in air of one-fifth of the low explosive limit, the gas is readily detectable by some person with a normal sense of smell."* The legislation states further that, *"to assure the proper concentration of odorant in accordance with this section, each operator shall conduct a periodic sampling of the combustible gases using an instrument capable of determining the percentage of gas in air at which the odor becomes readily detectable."*

Hence, odor fade is a potential hazard for safe distribution of natural gas.

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Odor Fade prevention

For the safety of all end-users of the pipeline gas, a pre-odorization step is required to saturate the new line with odorant before commissioning the line for service, so that odorized natural gas entering the new line remains adequately odorized upon reaching end-users.

The process of pre-odorizing or saturating the line with odorant is commonly called “pickling”.

Commissioning and pipeline conditioning can also be performed concurrently by supplemental odorization to compensate for odor loss.

New steel pipeline conditioning process will be complete when all the iron oxides sites will be reduced to ferrous sulfide.

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Instrumentation

- Sophisticated instruments (GC, Dräger tubes, chemiluminescence) can measure odorant concentration but cannot take into account odor masking, olfactory fatigue…

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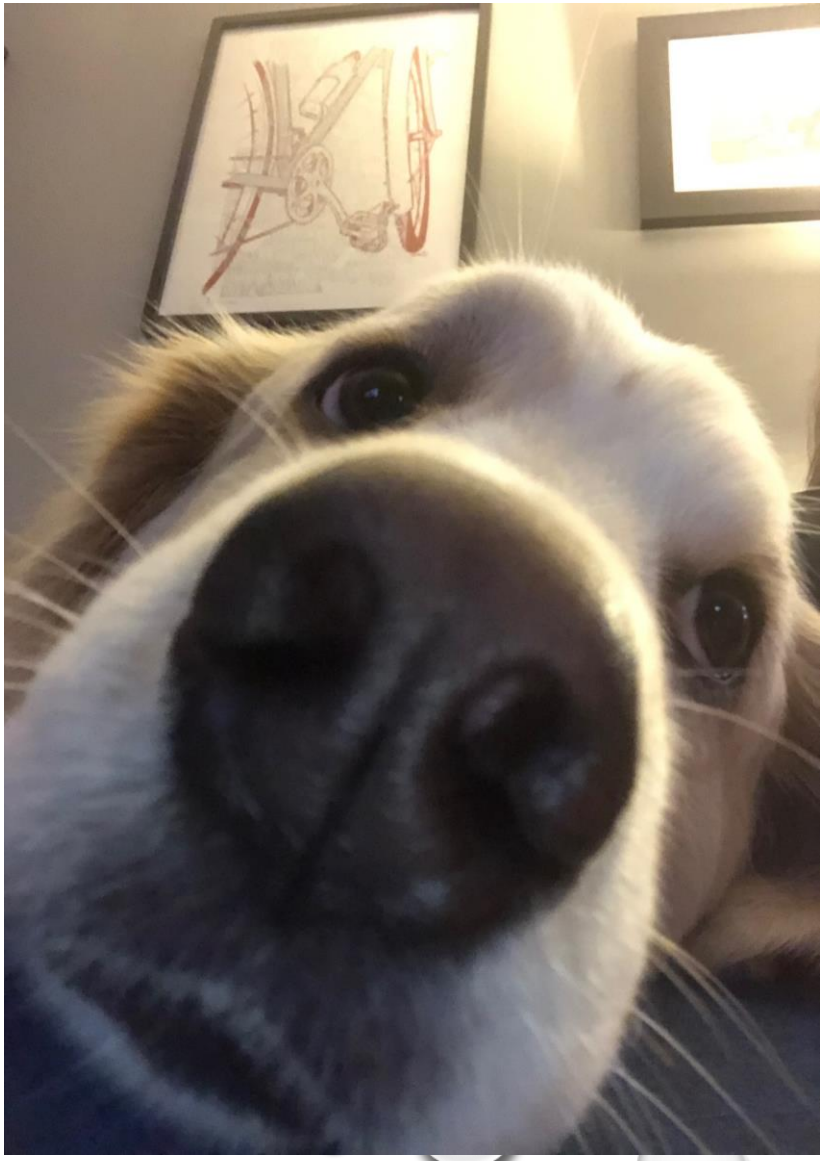
George



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Wes

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Pickling

GAS PIPELINE CONDITIONING

Disclaimer: The views of the pickle above may not reflect the view of MRR management

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Pickling: What is it and Why?

What is it?

1. Pipeline conditioning

Why?

1. Odorant absorbed by new pipe
2. Insurance for gas company
3. Ensures safety of customers

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Pickling: Objectives

1. Condition pipeline
2. Ensure the client can continue selling gas while pickling
3. Ensure customers receive adequately odorized natural gas
4. Complete project with no odorant release to atmosphere
5. When necessary, continuous monitoring of odorant levels in the pipeline

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Practical Approaches to Pipeline Pickling

1. Organized injection of odorant in pipeline proportional to flow (preferred) or proportional to time
2. Slugging of pipeline with odorant. Sometimes referred to as a “pre-soak” or off line conditioning

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Practical Approach to Counter Odor Fade

1) On-line conditioning

- Concurrent commissioning and pipeline conditioning
- Odorant is added to “pickle” the pipeline in an increasing stepwise fashion.
- All gas is sold – no venting, no flaring
- Slower process due to gradual increase of odorant concentrations
- More control measures are needed for success (sampling, gas flow)– higher risk
- Need to be able to move gas from front end to tail end of pipeline without gas stoppage.

Option 1: Odorizer at the front end, odorizer at tail end of pipeline
Option 2: Odorizer only at tail end, use odorized natural for “pickling”
Option 3: odorizer only at front end, if flaring of gas is possible at tail end until system is stable.

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Practical Approach to Counter Odor Fade

2) Off line conditioning

- Introduce odorant into pipeline while it is offline, after hydrotest/pigging process. Move odorant to tail end of pipeline by venting or flaring. Keep at low pressure ie 10-30 psig.
- Let pipeline pickle for 1-5 days.
- Flare down pipeline and start flowing gas as in scenario 1.
- Advantage – the first “pickling” phase is quicker to complete – lowers risk somewhat.
- Disadvantage – needs a downtime to complete prior to start of gas flow. Flaring gas is not desirable in some areas.

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Practical Approach to Counter Odor Fade

3) Considerations:

- Can I move gas to tail end of pipeline reliably?

  -mercaptan must be moved to tail end of pipeline for successful pickling. Challenge in low diameter, low flow pipeline.

- Can I maintain steady gas flow?

  -Often, natural gas clients will have variable gas flow upon startup. This will impact the mercaptan reaction with pipeline. Lower velocity → higher retention time → lower resulting mercaptan in gas

- Do we have customers between front end and tail end of pipeline?

  -When pipeline is not yet sufficiently pickled, it is often the case that high concentration of mercaptan are necessary at the front end in order to keep concentration at the tail end adequate. Mid point customers would get over odorized gas. Solution: keep 2 odorizers until pipeline is stable.

- Pipeline concentrations can drop out in a newly "pickled" line under very low flow conditions. Keep supplemental odorizers on hand to counter act this event.

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Practical Approach to Counter Odor Fade

4) Calculations/procedure:

- Measure baseline concentrations of natural gas in your system. Set a system target outlet concentration, i.e. 1.0 ppm TBM. Do odorometer reading before start of procedure.
- Set system target outlet acceptable range i.e. 0.8-1.5 ppm. Design a protocol of what to do in case system moves outside this range.
- Calculate the volume of natural gas in your pipeline at each operating pressure.
- Set startup pressure low if possible to shorten stabilization period.
- Calculate the retention time of natural gas at each operating pressure based on startup flows. Set the sampling frequency to match the gas velocity.
    - E.g. if 5 mile section is turned over in 10 hrs, a good sampling frequency would be 1x/hr at the beginning of process and 1x/10 hr when process is stable.
- Calculate surface area of pipeline. Apply 0.05 - 0.1 cc /ft^2 odorant dosage to pickle the pipeline. Inject this odorant after the nitrogen plug has been introduced. Measure/readjust. For low flow pipelines, inject odorant at low pressures i.e. 30 psig in order to stabilize system faster.

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Practical Approach to Counter Odor Fade

4) Calculations/procedure cont….

- If you have clients at mid point, you need to resort to off line conditioning. Ie prepare pipeline before putting into service OR have an odorizer feeding the mid point clients.
- Continue to inject supplemental odorant from 0.5 - 5 lbs/mmscf dosage. Measure/readjust.
- Increase dosage of front end odorizer until break trough has occurred.
- Tail end odorizer is odorizing unodorized gas at 0.5 lbs/mmscf
- Decrease tail end odorizer dosage as inlet concentration is increasing. Ie control downstream concentration to be at target eg 1 ppm or less than 0.5% gas in air
- Decrease front end odorizer dosage as concentration at tail reaches target.
- Shut off tail end odorizer if you can control pickling with front end odorizer.
- Decrease front end odorizer dosage until you achieve about 0.2 lbs/mmscf supplemental. At this time, attempt to shut off odorizer and measure system TBM.
- Keep both odorizers on site 2 - 4 weeks after the odorizer has been shut off to make sure system is stable.

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New section of pipe to be installed

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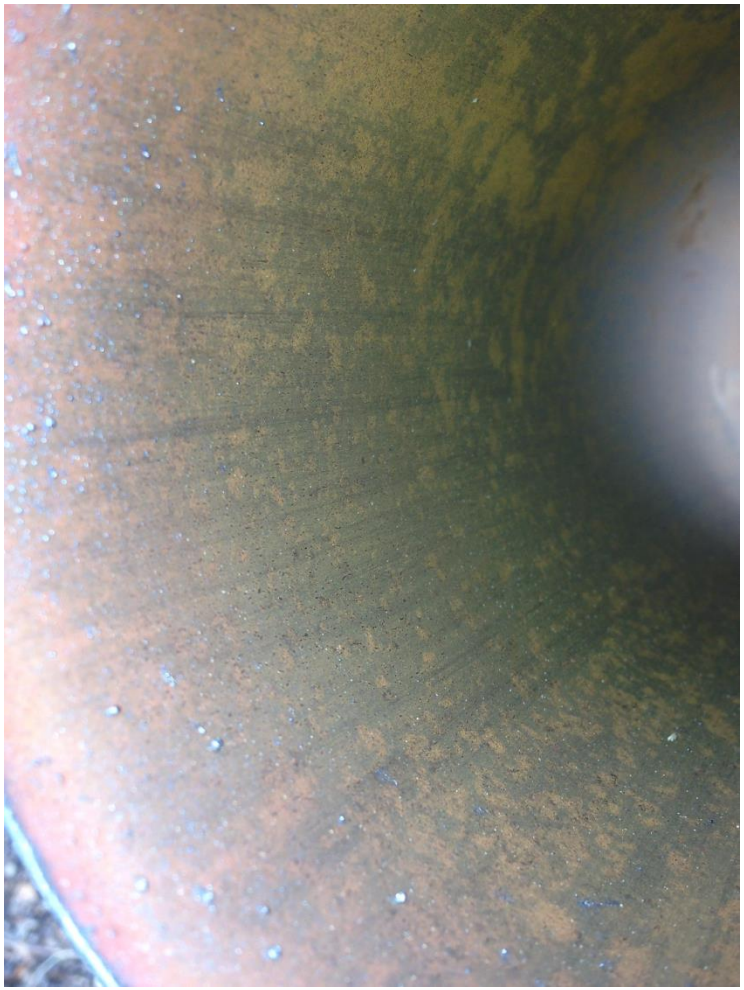
New section of pipe to be installed before and after foam pigs



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Sequential foam pig runs

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Last foam pig run

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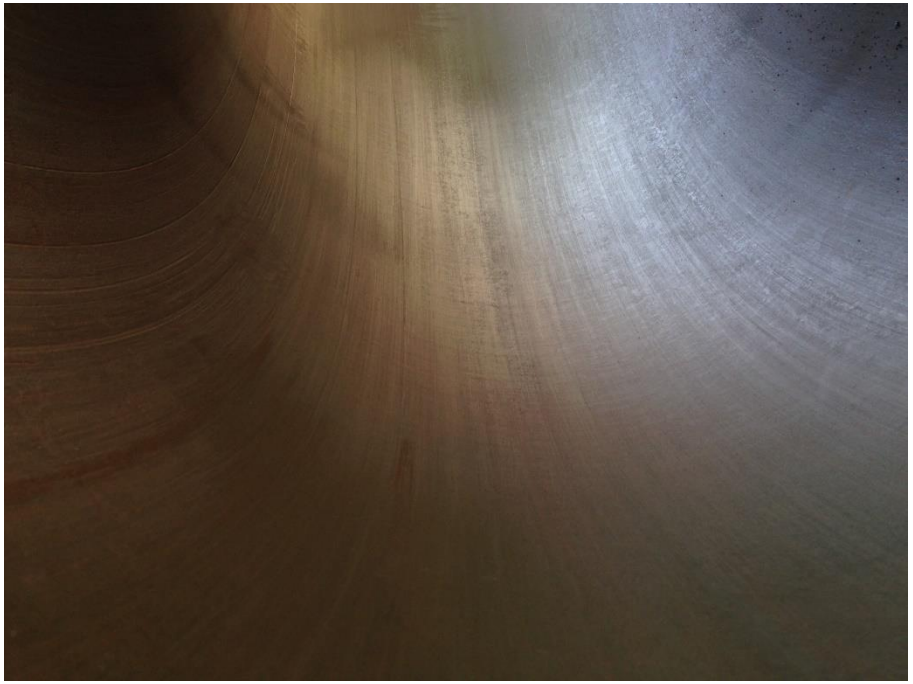
New section of pipe to be installed after brush pigs



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Tools/manpower needed

- Manpower – setup and operate odorizers (1 or 2 people), measure TBM conc. (1 person), odorometer reading (2 people, 24/7 for 1 week)
- Level/secure pad for odorizer or trailer.
- Odorizer – design with adequate min/max flowrates
- Odorant blend of the local distribution system. Volume of odorant for 1-2 months at 0.5lbs/mmscf + what is required for pipeline conditioning.
- Gas Flow meter (preferable)
  - Turbine flow meter with pulse output
  - Ultrasonic with 4/20mA flow output
- Injection and power gas taps (1/2”). Direct injection into pipeline for best results….no raisers or underground lines. Nitrogen power gas is possible.
- Power: Solar powered odorizer. Flowmeters can be battery operated or use pulse output turbine meters.
- Sampling taps (before, after and downstream)
- Measurement tools for odor (sniff test, stain tubes, GC, sampling bags)
- Odorant flow alarms to gas control (optional)
  - Via modbus
  - Via discrete general alarm and pulse flow ouput
- Odorant spill response kit.
- Large volume flare for moving gas (optional), small flare for sampling gas from underground risers (if needed).

120-gal skids

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Various installations depending on weather

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Various installations depending on size of pipeline.
1000 gallon setup vs 100 gallon setup

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MRR Odor Tracker
Used for Online Odorant Level Monitoring

Available features:

• GDS sampler (Class I Div1) stand-alone unit with Modbus, 4-20mA output options

•MRR OdorTracker C1D2 or C1D1

- Insulated aluminum enclosure
- RTU and cell modem
- Natural gas outlet filter
- Optional catalytic heater

Available in simplified stand-mounted version

Optionally powered by 120VAC, 24VDC or solar panels

Configurable sample intervals from 1 hour to 8 hours

E-mail/text alarms on out-of-range odorant levels

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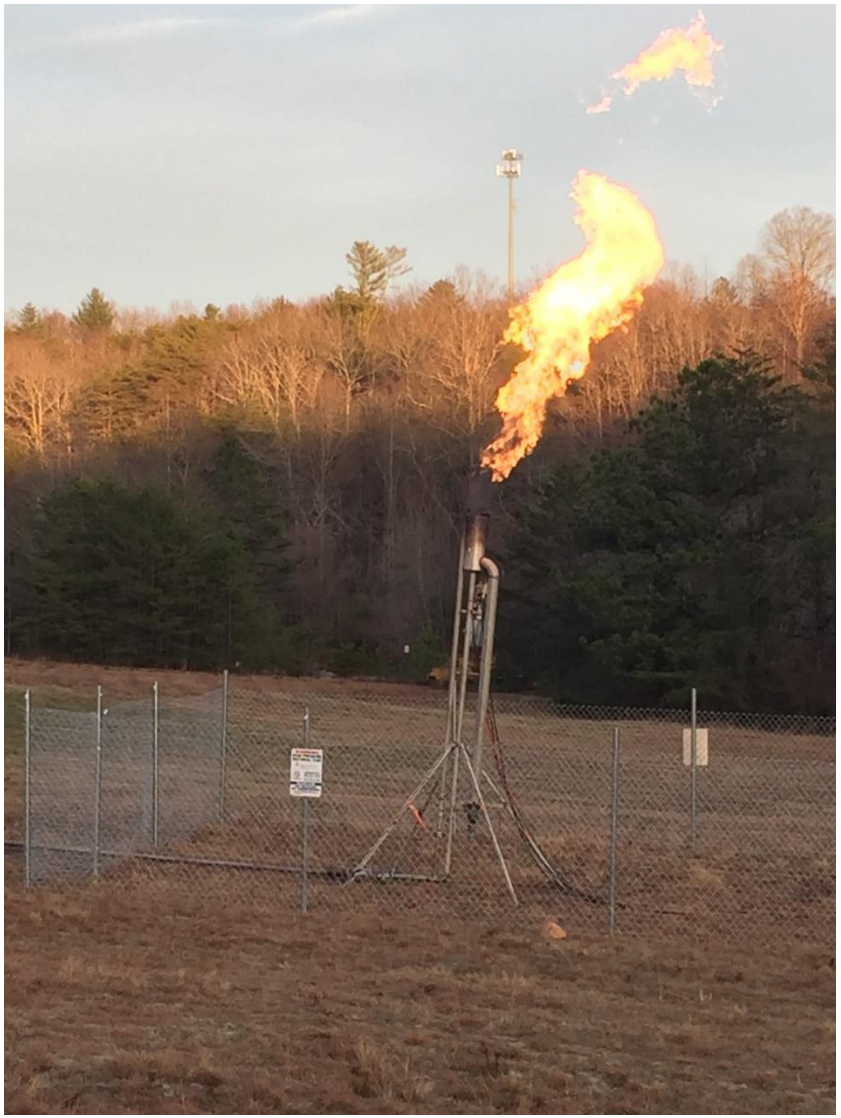
Ways to Create Flow

Industrial heaters



Flare

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Ways to Create Flow cont.

Flameless Flare

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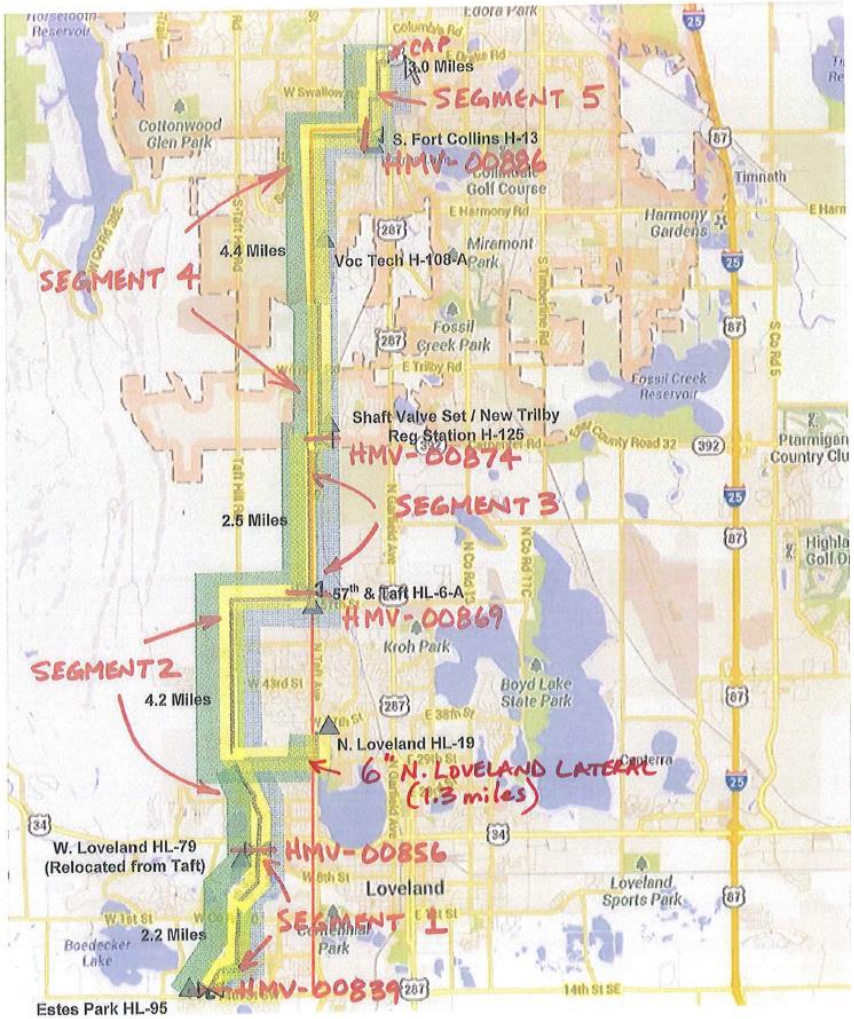
Case Study 1 (the good)

16” steel pipeline – 10.3 miles.



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Case Study 1

16“ steel pipeline, 10.3 miles long, 760 psig, 100-400 mscfh

Odorant : Scentinel E

INPUTS							
Pipeline diameter	D	16	inches				
Pipeline length	L	54384	ft		convert	10.3	miles =
Pipeline pressure	P	760	psig				
Gas flow - Low	Q(lo)	0.1	MMSCFH				
Gas flow - High	Q(hi)	0.4	MMSCFH				
Baseline odorant dosage	BD	0.9	lbs/MMSCF				
Pickling dosage	PD	0.1	cc/sqft				
Odorant density	rho	6.74	lbs/gal				
OUTPUTS							
Pipeline inner surface area	A	227803	ft2				
Pipeline volume (vol of gas at actual P)	V	75934	ft3				
Standard volume of gas in pipeline (vol of gas at atmospheric P)	Vs	4001794	ft3				
Residence time at LOW flow	T(lo)	40.0	hrs				
Residence time at HIGH flow	T(hi)	10.0	hrs				
Baseline daily odorant input at LOW flow	W(lo)	2.16	lbs/day	or	0.3	gal/day	
Baseline daily odorant input at HIGH flow	W(hi)	8.64	lbs/day	or	1.3	gal/day	
Odorant for breakthrough	M	40.6	lbs	or	6.02	gal	

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Case Study 1 Cont.

Front end odorizer in a Conex box – needed for 4-8 weeks to pickle pipeline.

Ran in a proportional to flow injection mode using ultrasonic Siemens clamp on meter.

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Case Study 1 Cont.

Tail end odorizer – was needed for 24hrs to odorize incoming unodorized natural gas until breakthrough occurred.

Ran this unit on a timed injection for 24 hrs.

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Case Study 1 Cont.

Tail end Odor Tracker– needed for 4-8 weeks to pickle pipeline.

Automated sampling 1x/hour.

Solar powered

Measuring TBM concentrations

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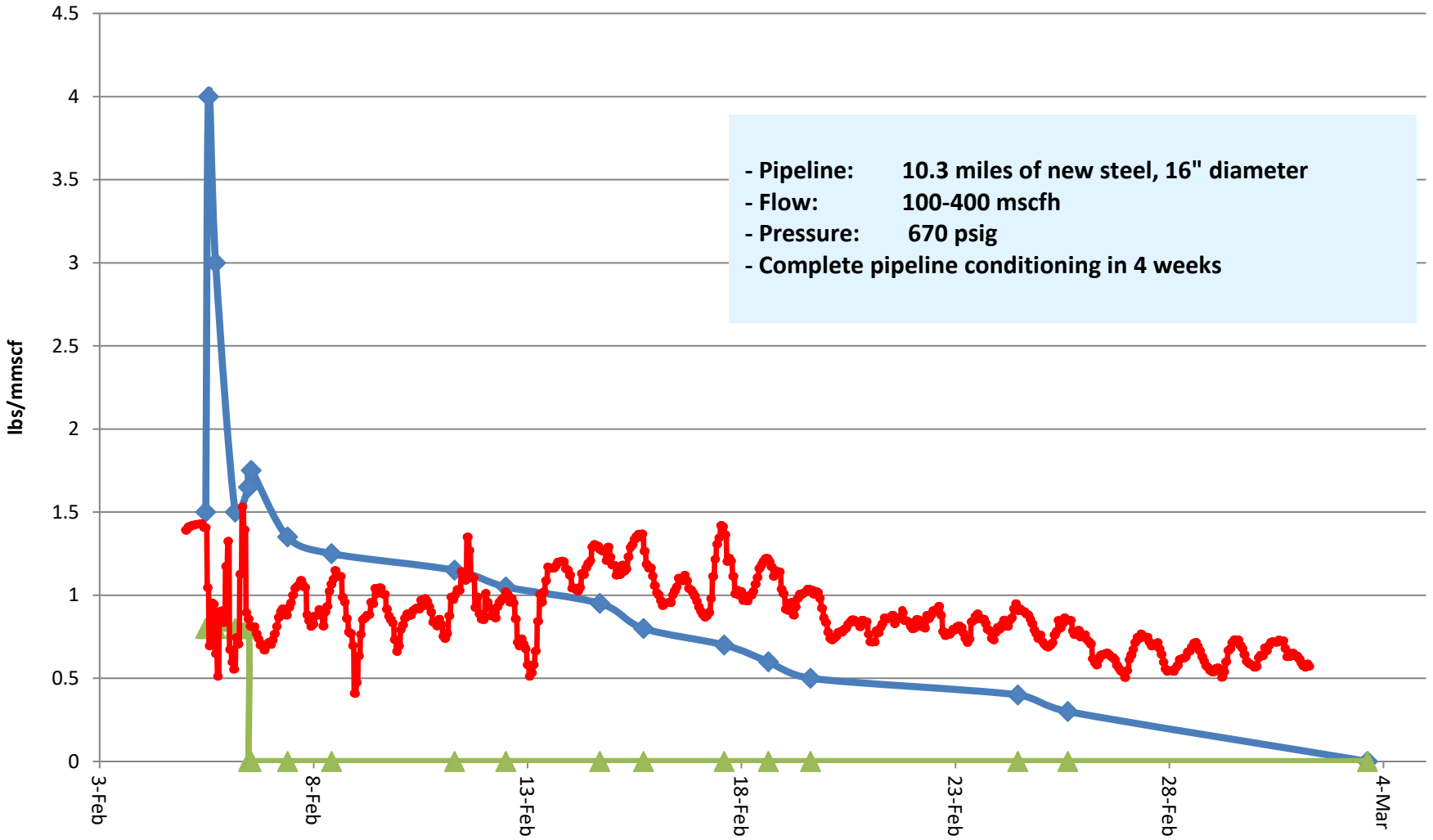
Case # 1 Pickling Data

Supplemental Injection Rates (Front-End, Tail-End) & Tail-End Odor Level Trends



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Case Study 1 Summary

Process step	Amount of supplemental odorant used (lbs)	Dosage at tail end (lbs/mmscf)	Dosage at front end (lbs/mmscf)	Duration	Odorant dosage (cc/ft^2)
Initial flow until breakthrough	30	0.8	1.5	1 day	0.075
Injection to complete project	110	0	1.5 decreasing to 0	30 days	0.27
Total	140				0.345

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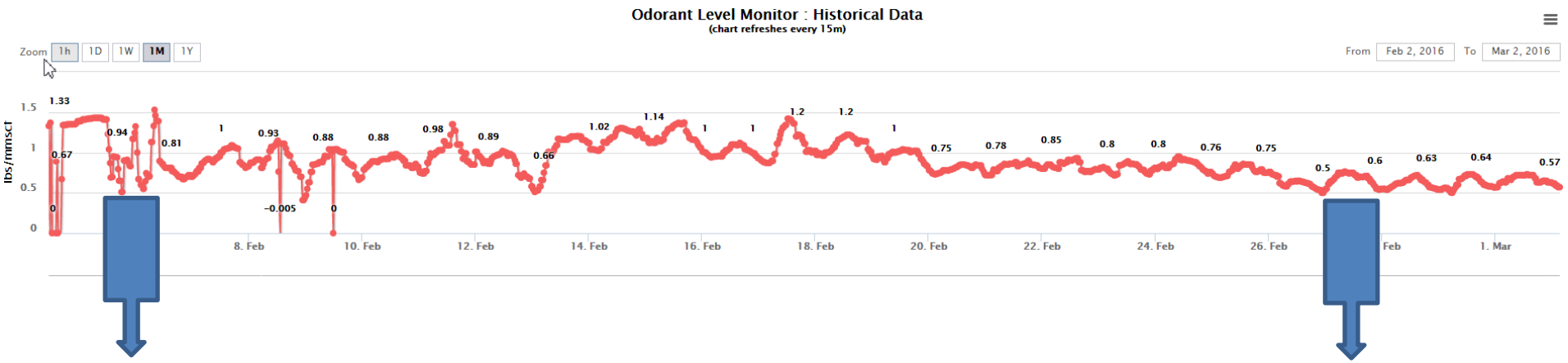
Case Study 1 Tail end Concentrations

16 " pipeline, 10.3 miles long. 760 psig, 100-400 mscfh.

Odorant : Scentinel E.



Tail end odorizer was required only for 24 hrs.

Starting Feb 7th, the front end odorizer took over the pickling process

Variability in tail end concentrations is due to daily load flow fluctuation. The higher the retention time in the pipeline, the more the mercaptan gets reacted with iron oxides

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Case Study 1

Challenges:

1. Maintain target odor levels at tail end with the disulfides and new pipeline smell . Had to increase dosage at tail end to 1.0 lbs/mmscf to get good smell.
2. One 12 hr period - good MSA stain tubes readings were not matching odorometer readings. We concluded a mixture of olfactory fatigue and background masking were causing this effect. We temporarily started the tail end odorizer to add fresh odorant to the background, smell , relying on the odorometer readings at the sales point and in distribution to make final decisions. CAUTION!
3. Manpower – 24/7 sniff testing for 3 days, then 1 month after at a daily rate.
4. Maintain continuous power to Siemens clamp on meter.
5. No 24/7 monitoring of odorizer. Odorizer needs to be well setup and checked periodically. (ie 2x/day minimum) It would be recommended to setup a remote monitoring to gas control via modbus or discrete alarm signal ie MRR Odor Tracker (1x/hr automated sampling and measurement tool for TBM)
6. Back-up odorization would be recommended.

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Case Study 1 Cont.

Successes:

1. Very short time to put line into service → 2 days. Well below industry average. Clean pipeline and good installation procedures!
2. Numerous sampling points → good control
3. Enough manpower → fast response time, no stoppage of gas flow

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Case Study 2 (the bad)

6“ steel pipeline, 5.3 miles long, 500 psig, 1 - 10 mscfh

Odorant : Scentinel F-25

Front end odorizer

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Case Study 2

Solar powered tail end odorizer, flowmeter and OdorTracker

Case Study 2 Summary

- Challenge: natural gas client had 4 boilers with designed usage for 100 mscfh. However, due to delays of certification and equipment problems, the startup of main boiler was delayed by 1 year. Only the smallest boiler 1-2 mscf was being used intermittently (no flow for 2 days, then flow for ½ day)
- Upon start up, the residence time was between 4-8 days.
- Odor loss occurred all year, with no possibility of pickling the pipeline under low flow and intermittent flow conditions. Natural gas was sold during that year, but supplemental odorization had to occur at all times.
- Project costs increased significantly. Temporary odorization for extended periods is not desirable due to increased risks to gas company (exposed equipment and pipeline)

- Solution: eventually, pipeline was put out of service and an offline pickling procedure was applied.
- Recommendation: Newly installed low flow or intermittent pipelines should apply an offline conditioning method.

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Case Study 3 (the interesting)

24“ steel pipeline, 12 miles long. 170 psig, 200 mscfh

Odorant : Scentinel S-20

Front-end odorizer

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Case Study 3

Residential area

Underground vault

Secured injection equipment

Tail-end odorizer

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Case Study 3 Summary

- Challenge: Natural gas client had new pipeline in residential area. The risk of fugitive odor had to be engineered. The area had also theft and vandalism concerns.

- Solution: Installation of equipment inside steel ConEx boxes. All connections (liquid injection, gas connections, electrical, communication) were made below grade, with no exposed piping or connections.
- 24/7 security was provided for the project.
- MOCII buildings were installed to continuously apply negative pressure on the odorization buildings.

This 12 hour retention time pipeline was pickled in 6 weeks. We allowed 2 weeks for validation before demobilizing equipment.

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Case Study 4 (the ugly)

8“ steel pipeline, 16 miles long. 125 psig, 7,000 - 18,500 mscfh

Odorant : Scentinel E

Front end odorizer

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Case Study 4 Cont.

Midpoint odorizers

Midpoint injection

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Case Study 4 Summary

Process step	Amount of supplemental odorant used (lbs)	Dosage at midpoint (lbs/mmscf)	Dosage at front end (lbs/mmscf)	Duration	Odorant dosage (cc/ft^2)
Initial flow until breakthrough	26	24	6	6 days	3.86
Injection to complete project	1483	0	12 decreasing to 0	359 days and still ongoing	Still ongoing
Total	1509				Still ongoing

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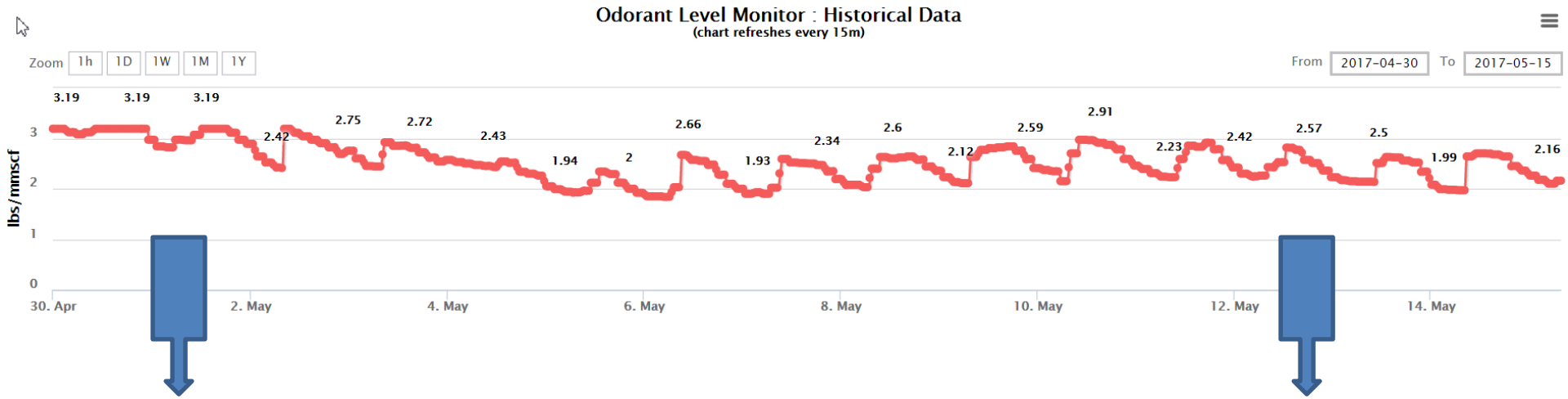
Case Study 4 Tail end Concentrations

8” pipeline, 16 miles long. 125 psig, 7,000 – 18,500 mscfh.

Odorant : Scentinel E.



Midpoint end odorizer was required for 44 days.
Starting March 2nd, the front end odorizer took over the pickling process

Variability in tail end concentrations is due to daily load flow fluctuation. The higher the retention time in the pipeline, the more the mercaptan gets reacted with iron oxides

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Case Study 4

Challenges:

1. Extremely low flow conditions – used flare to create actual flow
2. Local permitting issues
3. Maintain target odor levels at tail end with the disulfides and new pipeline smell. Had to increase dosage at tail end to 1.0 lbs/mmscf to get good smell.
4. Manpower – Readings every 4 hours for 11 months!!!
5. Clamp on flow meter fluctuations due to constraints on where to install.
6. Quality of the pipeline unknown
7. No pig launch/receiver built into pipeline design

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Case Study 4 Cont.

Successes:

1. Numerous sampling points → good control
2. Enough manpower → fast response time, no stoppage of gas flow

Solutions:

1. Install permanent low flow odorizer due to pipeline conditions
2. Bring in temp CNG to run line while temp pig launch/receiver installed and pipeline pigged

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Thank you!