What You Should Know About Odor Fade and Pickling

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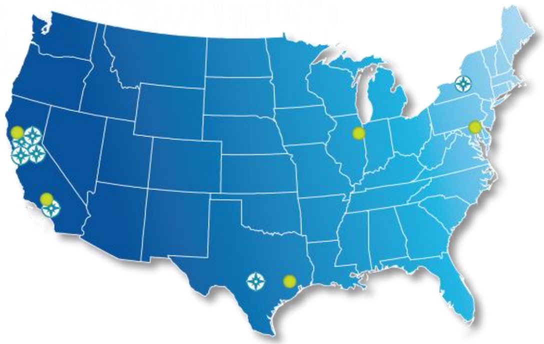

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Topics for Today

- What is odorant fade and odor masking?
- Lab testing of odorant fade
- Modeling the dispersion of odorant entering a pipeline
- Coating + low flow study with TBM and THT odorants

- Sponsored by Operations Technology Development (OTD)
  - A collaborative group of utilities and pipeline companies
- First study sponsored by DOT/PHMSA

Topics for Today

What is odorant fade and odor masking

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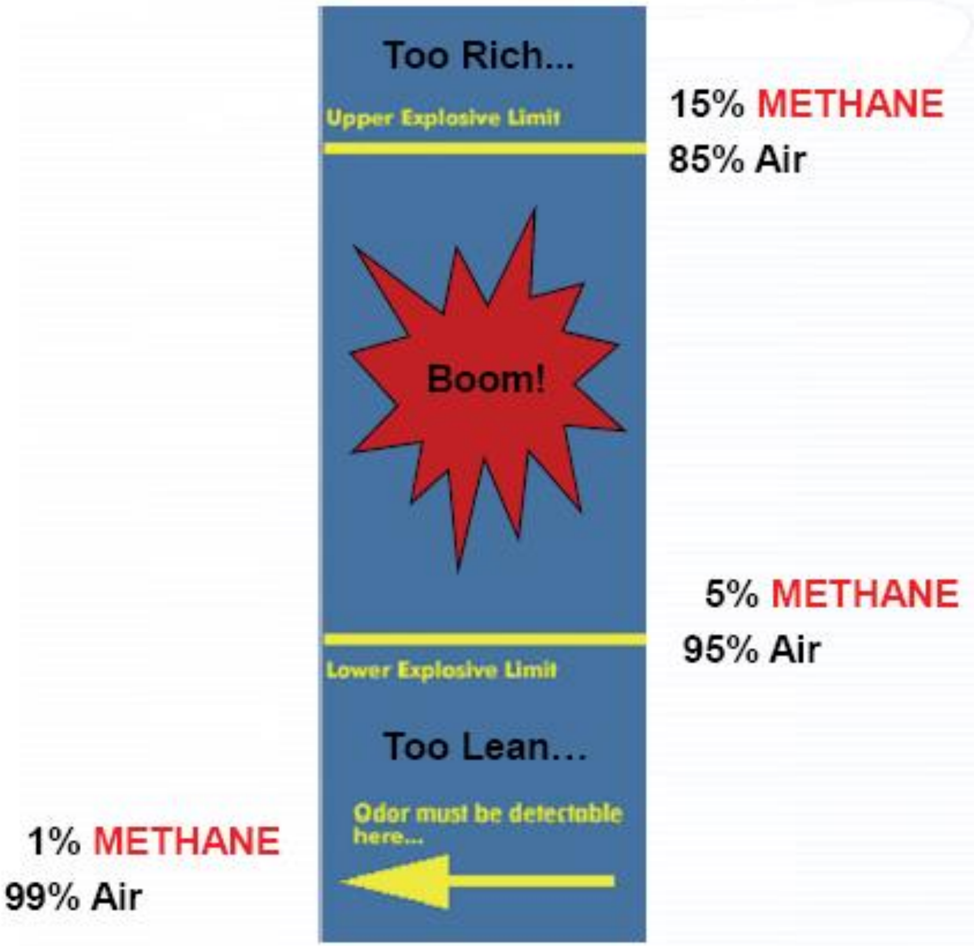
Coating/low flow study with TBM and THT odorants.

Why is Natural Gas Odorized?

- The composition of natural gas is mostly methane (usually > 90%), with decreasing levels of other hydrocarbons, carbon dioxide, nitrogen, and other diluents.
- Because of this composition, natural gas is mostly odorless.
- At certain concentrations natural gas can be dangerous.
  - 5-15% is the range for the lower and upper explosive limits of methane in air
- For the safety of those who live and work around natural gas, chemical odorants are introduced into natural gas, allowing its presence to be known.

Explosive Levels Explained



- > At concentrations greater than 15%, the mixture is too rich and there is not enough oxygen to support combustion.
- > At concentrations less than 5%, the mixture is too lean and there is not enough combustible material to support combustion.
- > Between 5% and 15% the mixture is "just right".

Federal Code Requirement to Odorize Gas

- **§ 192.625 Odorization of gas.**
- (a) *A combustible gas in a distribution line must contain a natural odorant or be odorized so that at a concentration in air of* ***one-fifth*** *of the lower explosive limit, the gas is readily detectable by a person with a normal sense of smell.*

Note: LEL for natural gas is 5% gas-in-air.
One fifth = 1% gas-in-air
One tenth = 0.5% gas-in-air

- Odorants have been added to natural gas streams in the United States ever since the 1937 Texas school explosion

State vs Federal Requirements

- State Jurisdictions may have even more stringent requirements:

MA - 0.15% gas-in-air

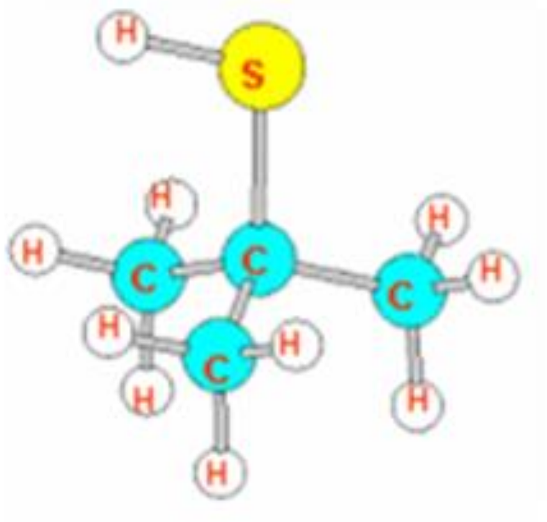
NY - 0.5% gas-in-air (Distribution) / 1% gas-in-air (Transmission)

NH - 0.8% gas-in-air

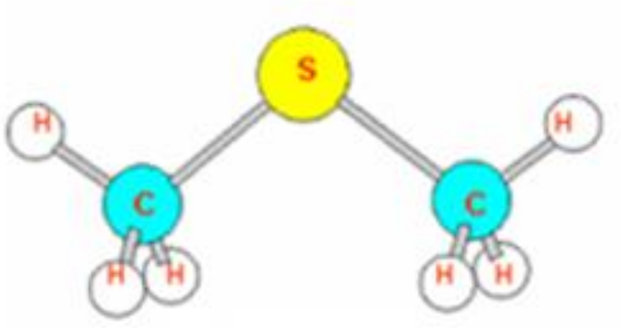
How Gas is Odorized

- Odorants used in the gas industry in the U.S. all contain sulfur, carbon, and hydrogen and belong to a category of chemicals known as organosulfurs.
- There are three general classes of organosulfur compounds:

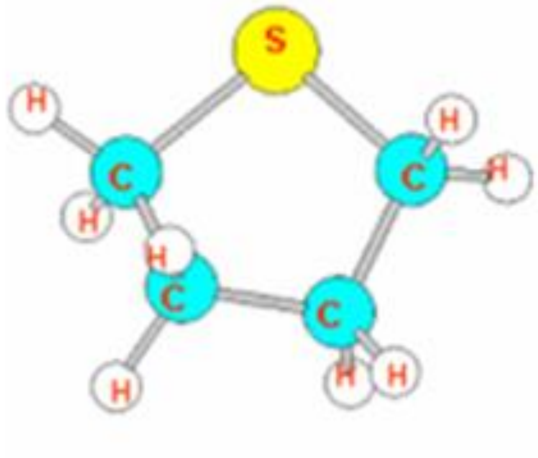
Mercaptans | Alkyl Sulfides (Thioethers) | Cyclic Sulfides



t-butyl mercaptan (TBM)



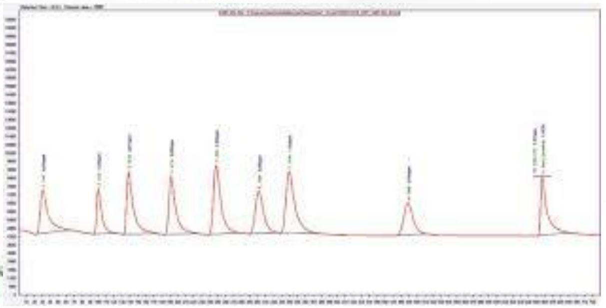
dimethyl sulfide (DMS)



tetrahydrothiophane (THT)

How Odorant is Measured

- Odorant Chromatograph – continuous monitoring, data seen in Gas Control Centers
- Odor Handy portable device
- Portable Odorometer for sniff test
  - Relies on human olfactory system
  - Gives ability to spot check at various points
  - Requires a “calibrated” nose
  - Meets legal definition of odorized gas
  - Normal sense of smell can be affected by many things



Odorant Fade vs Odor Masking

- Odorant Fade: the loss of odorant by physical or chemical processes inside the pipeline.
  - Surface interactions of odorant with the pipe (adsorption or absorption)
  - Scrubbing/dissolution by condensate or cleaning liquids
  - Chemical reaction/oxidation of odorant with other components
- Odor masking: the change in perception of the characteristic gassy smell of odorants present in natural gas.

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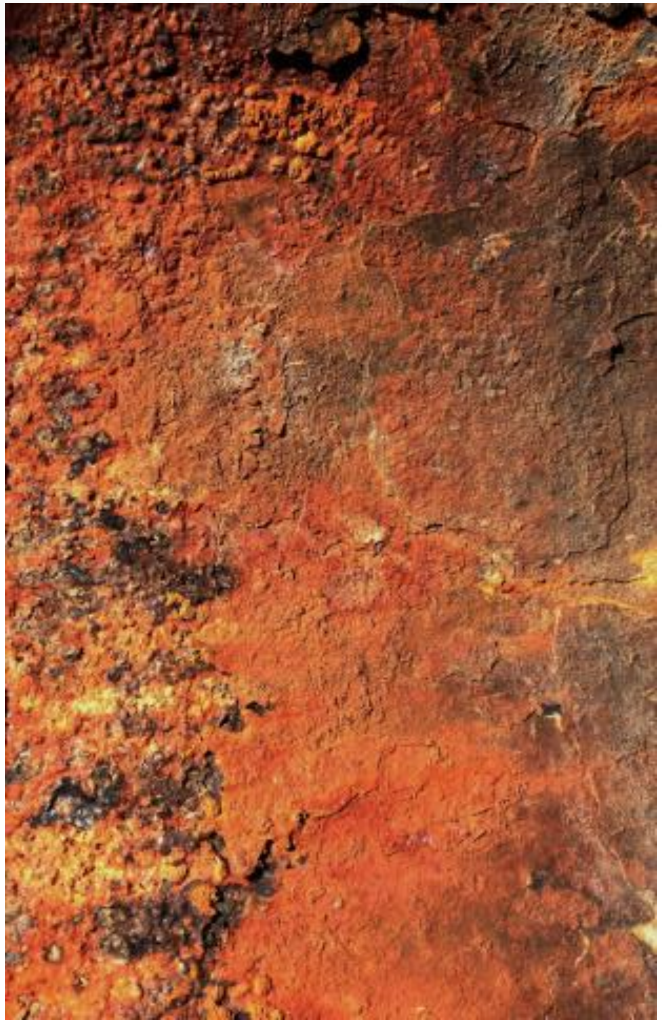
Typical Odorant Interactions – Adsorption

- **Adsorption** is the process by which a gaseous molecule or particle is physically attracted to and adheres to a surface.
- This adherence is caused by weak van der Waals forces or electrostatic forces (surface charge interactions) generating a physical attraction to a surface, and is usually reversible.
- The driving force for adsorption is the ratio of the partial pressure and the vapor pressure of the compound.
- Adsorbability of a compound increases with increasing molecular weight, a higher number of functional groups such as double bonds or sulfur compounds, and increasing polarization of the molecule.

Typical Odorant Interactions – Absorption

- **Absorption** is the filling of pores in a solid, or dissolution into a liquid.
- The substance being absorbed is physically taken up by the bulk material and is partitioned between the gaseous phase and the solid or liquid phase.
- Odorants be physically absorbed into plastic, hydrocarbon condensates, or other liquids/solids that may be present in steel or plastic pipelines.
- Condensates may be present due to “oil fogging” of new pipe, cleaning activities, addition of hydrocarbon to mitigate elastomer seal shrinkage, and exceeding the hydrocarbon dewpoint of a gas high in heavier hydrocarbons.

Typical Odorant Interactions – Oxidation



- > **Oxidation** is when the odorant chemically reacts with rust present on steel pipe, although any oxidizing compound promotes the reaction.
- > The rust derives from the process used to manufacture pipe for the natural gas industry.
  - All hot-rolled steel products contain mill scale on the outer surfaces.
  - Bluish black form of iron oxide commonly called magnetite (Fe_3O_4) and contains iron in both the +2 and +3 valence state.
  - Breaks in the mill scale allow rusting to occur.
  - Rust consists of hydrated iron(III) oxide ($Fe_2O_3{\cdot}nH2O$) and iron(III) oxide-hydroxide ((FeO(OH) and $Fe(OH)_3$), all having a characteristic reddish orange color.

Typical Odorant Interactions – Oxidation

- As a result of the production process, the interior wall of new steel pipe contains very reactive rust and mill scale, which will react with mercaptan-based odorants to form less odorous disulfide compounds, magnetite, and water.
- Not only do the disulfides possess lower olfactory impact than mercaptans, they have much lower vapor pressures so will be more likely to adsorb on pipeline surfaces.

$$2\ RSH + 3\ Fe_2O_3{\cdot}nH2O \rightarrow RSSR + 2\ Fe_3O_4 + (n+1)\ H_2O$$

$$2\ RSH + 6\ FeO(OH) \rightarrow RSSR + 2\ Fe_3O_4 + 4\ H_2O$$

$$2\ RSH + 6\ Fe(OH)_3 \rightarrow RSSR + 2\ Fe_3O_4 + 10\ H_2O$$

Odorant Fade – Not a New Problem

> Five cases where the odor of natural gas was questioned:

- 2009 explosion at the ConAgra Slim Jim Plant in Garner North Carolina, killing four, severely burning three, and sending sixty-seven people to the hospital;
- 2008 explosion at a Hilton Hotel under construction in San Diego, California that injured fourteen people;
- 2007 explosion at a hotel in Cheyenne, Wyoming, that severely burned two plumbers;
- 2005 school explosion in Porterville, California, burning two plumbers;
- 1999 explosion at a Ford power plant in Dearborn, Michigan, killing six, injuring thirty-eight, and causing $1 billion in property losses.

U.S. CHEMICAL SAFETY BOARD

What is Odor Masking?

- Change in perception of the characteristic gassy/sulfur smell of odorants present in gas.
- Observed when a chemical analysis of the gas indicates added odorants are present at typical values but are not detectable by a nose because another chemical is present that
  - reduces the odor intensity,
  - changes the characteristic odor,
  - or both.
- Masking issues are often transient making identification difficult

<u>How Do People Detect and Recognize Odors?</u>

- Human beings detect and recognize odors by a complex set of physiological and biochemical processes.
- Detection begins when odor molecules enter the nose and attach to areas in the nose called “odor receptors”.
- By precisely fitting into the odor receptors, the odor molecules cause an electrical signal to reach the brain. The brain translates the electrical signal and allows us to recognize the particular odor.
- Depending on the strength of the electrical signal, we sense a weak or a strong odor.
- Humans can distinguish more than 10,000 different smells (odorants)

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Overcoming Odorant Fade

- To overcome odorant fade, operators generally add extra odorant to supplement existing concentrations. In conjunction with this, natural gas flow rates can be increased to purge more gas.
- Decisions vary from company to company and are often anecdotal at best.
- Pre-planning and evaluation of system variables is key to avoid potential for fade.
- Engineering should work collaboratively with Operations, Gas Control, and I&R (Instrumentation & Regulation) to evaluate variables and build a plan.
- Use correct injection volumes, inject slowly or use a diffusion odorizer to achieve saturation of flowing gas – avoid "*dump & run*" techniques
- Wick type odorizers can be used for extended operations

Chemical Stability Parameters Tested

- Series of tests were conducted in 304 stainless steel gas sampling cylinders that were inerted with a silicon-containing coating on the interior of the cylinder.
- These containers were designed to be used as "control reactors" for comparison with results obtained with standard industry chemicals.
- TBM used because it has high reactivity.
- MEA selected as a surrogate amine compound representing volatile amine compounds used for natural gas treatment and as a constituent in hydraulic fracturing fluids.

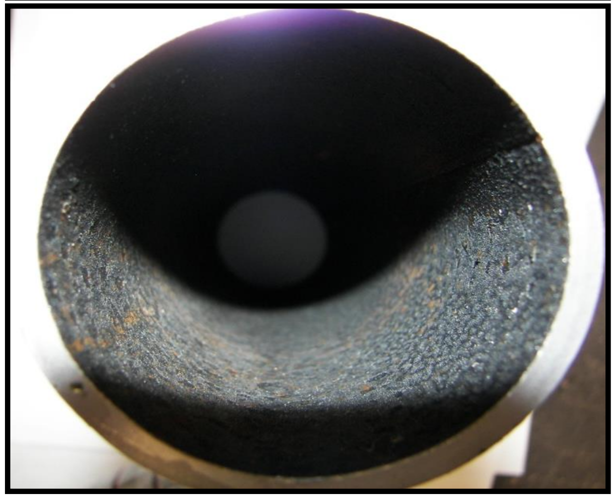
Parameter/Variable	Value or Range
Corrosion Level	None (i.e., passivated)
Gas Pressure	60 psig
Temperature	70°F
TBM	2 ppmv
Water	141 ppmv (~7 lb./MMSCF)
Oxygen	300 ppmv and 1000 ppmv
Hexanes	1000 ppmv (0.1 mole %)
Methanol	19 ppmv, 152 ppmv
Amine (MEA)	21 ppmv, 60 ppmv
CH_4	Balance

Chemical Interaction Results

- Results from these experiments showed there was no TBM odorant fading in the presence of
  - Up to 1000 ppmv oxygen,
  - 19 ppmv methanol,
  - 1000 ppmv hexanes,
  - 141 ppmv water.
- There was evidence of TBM odorant fade in the presence of
  - 152 ppmv methanol and
  - ~60 and 21 ppmv monoethanolamine (MEA).

Rust in Steel Pipe Results

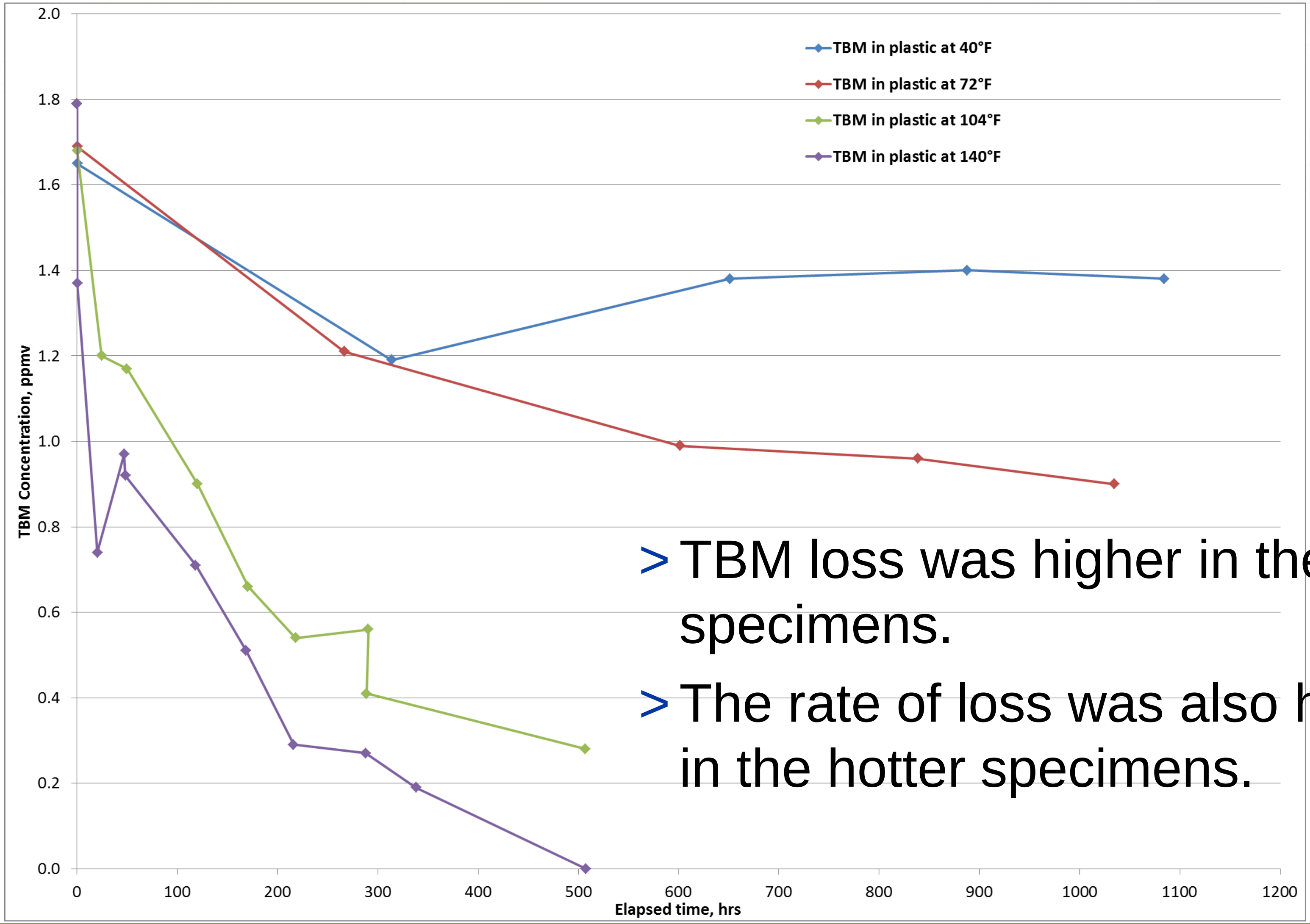
- Off the shelf pipe and pipe previously used for natural gas service were studied.
- TBM in methane added and odorant concentration was monitored.
- Results confirm expectations that the variable that most impacted TBM concentration in the gas phase was the presence of rust on the pipe surface.
- The concentration of TBM in the rusty steel pipe faded very rapidly until active sites were quenched.
- However, even the non-rusty pipe experienced odor fade.



Quenching with Liquid TBM

- Testing with liquid TBM injected to quench a used rusty pipe also showed a rapid loss of TBM.
- In a private communication with a pipeline company, an odorant application rate of 0.25 ml per square foot of internal pipe surface area was reported as being used for their pipeline conditioning. This rate was based on the amount of odorant estimated to be required to create a wall film thickness of 0.254 micron.
- We decided to initially use approximately ¼ the amount per injection.
- By the fourth cycle, the initial rate of TBM decrease had slowed to less than a fourth of the initial average rate, confirming that the active sites were gradually being depleted.
- The anecdotal application rate seems reasonable.

Does PE Pipe Also Lose Odorant? Lab Data with TBM



- TBM loss was higher in the hotter specimens.
- The rate of loss was also higher in the hotter specimens.

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Modeling the Dispersion of Odorant Entering a Pipeline

- Used ANSYS® Fluent®, a fluid flow simulation software package.
- GTI performed steady state Computational Fluid Dynamics (CFD) analysis to understand the effect of the odorant droplet mixing within natural gas pipelines at varying pressures, diameters and droplet sizes.
- A lean representative natural gas composition was used for the odorant mixing analysis.
- The odorant modeled is a 50/50 mixture of TBM and THT (by mass)
- Calculated a mixing quality as the gas/odorant mixture flowed downstream the pipe

Effect of Pipe Diameter – 50 Micron Droplet Size

- Larger pipe diameters (and corresponding greater gas velocity) requires greater length for mixing due to the time required for the droplets to disperse into the large pipe.
- The maximum length required with these data sets is 80 times the pipe diameter.

Pipe Diameter	Pressure, psig	Gas Velocity, ft/sec	Pipe Lengths for TBM	Pipe Lengths for THT
2"	60	0.2	10	10
4"	45	1	50	50
6"	200	5	50	50
8"	800	8	50	50
12"	250	15	50	50
24"	800	30	80	80

- As a safety factor a length of 100 pipe diameters is minimally recommended for sample collection and transition into non-metallic components.

Droplet Diameter Effect with Different Pipe Conditions

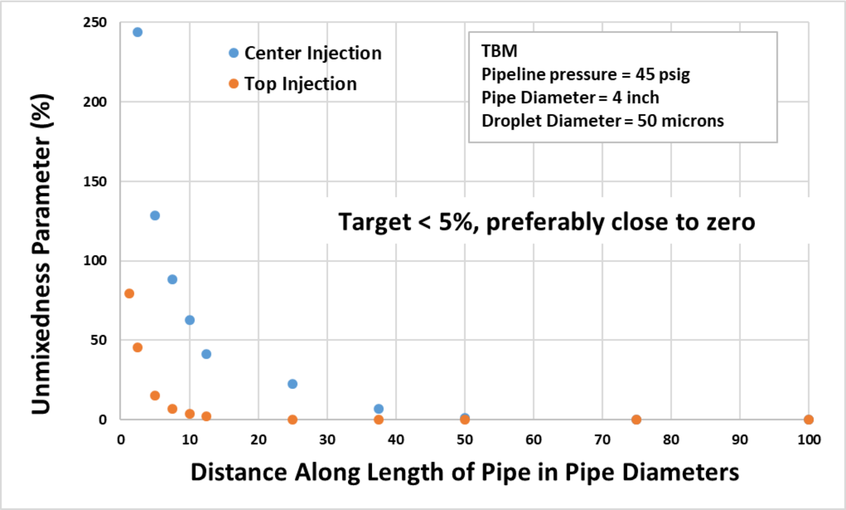
- The larger the droplet size, the longer is the mixing time needed for each of the pipe diameters and pressure.
- Increasing the pipe diameter increases the mixing length.
- Again, approximately 80 diameters needed for best mixing.

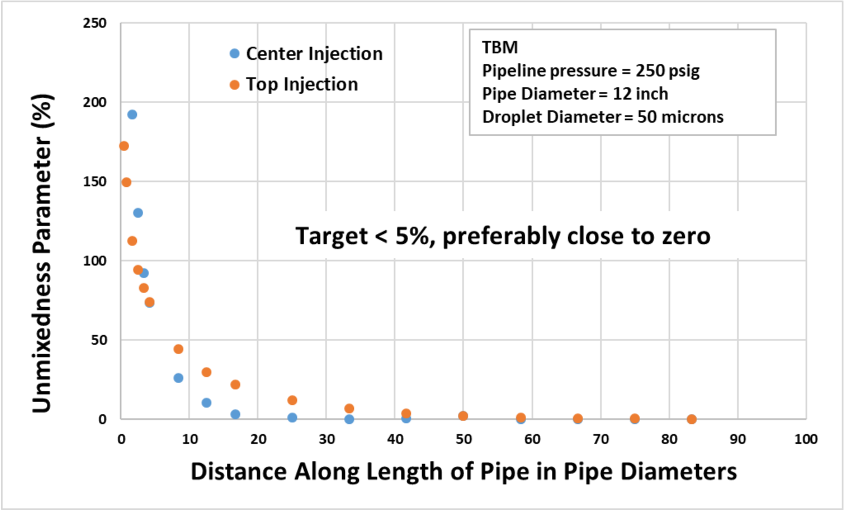
Pipe Diameter	Pressure psig	Gas Velocity, ft/sec	Odorant	Pipe Length for Mixing		
				50 Microns	200 Microns	300 Microns
2"	60	0.2	TBM	10	10	10
			THT	10	10	13
4"	45	1	TBM	50	50	50
			THT	50	50	50
6"	200	5	TBM	50	50	67
			THT	50	50	67
8"	800	8	TBM	50	50	75
			THT	50	50	75
12"	250	15	TBM	50	50	75 (est.)
			THT	50	50	50
24"	800	30	TBM	80	83	83
			THT	80	83	83

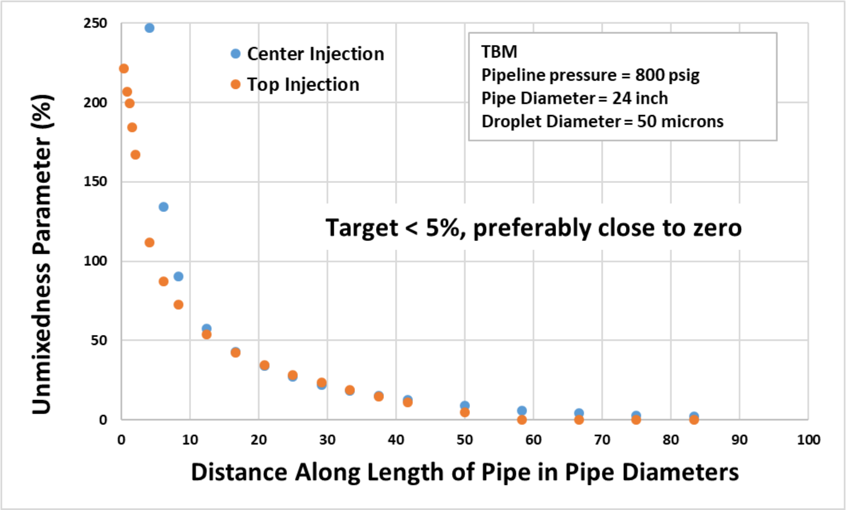
- As a safety factor a length of 100 pipe diameters is minimally recommended for sample collection and transition into non-metallic components.

Effect of Injection Location on TBM Odorant Mixing

- What would happen if the odorant was injected at different locations?
- Results from these three cases indicate that location does not have an impact on mixing for TBM.
- THT is expected to vaporize similarly or quicker since its vapor pressure is lower than that for TBM.







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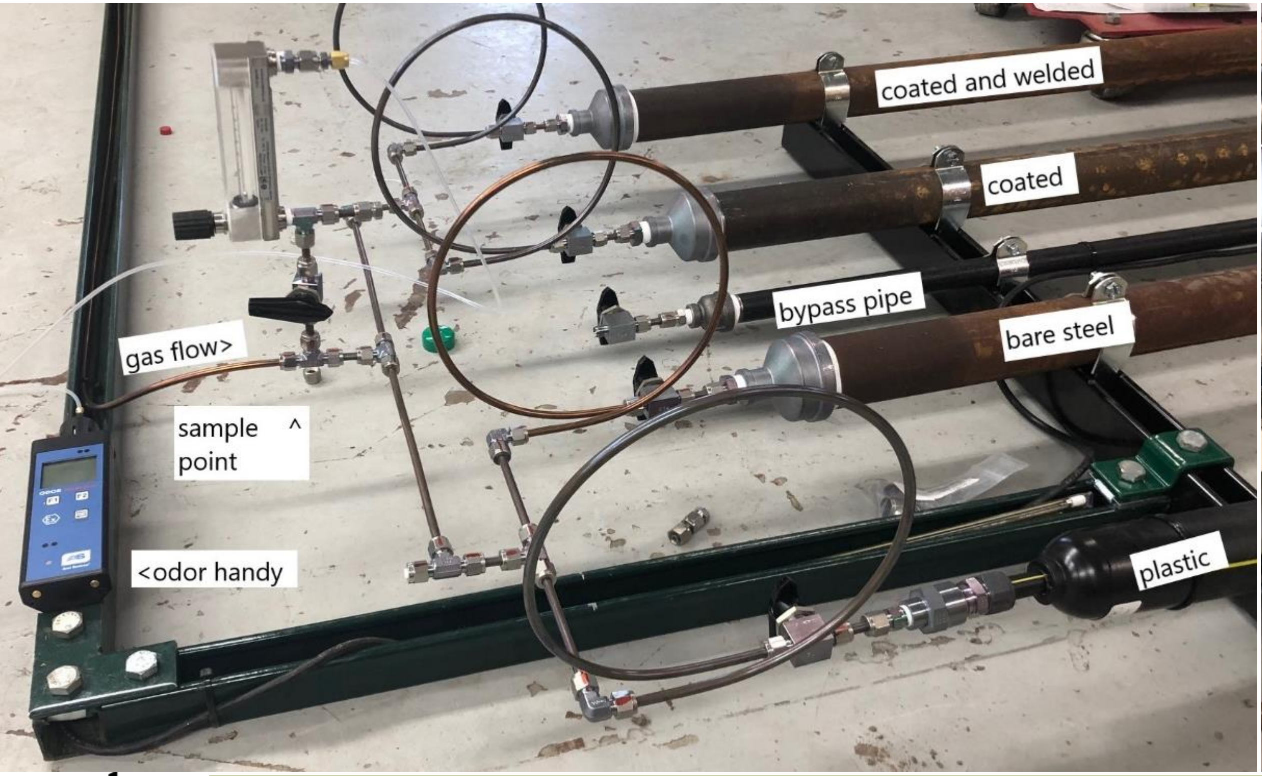
Odorant Fade and Low Flow Issues

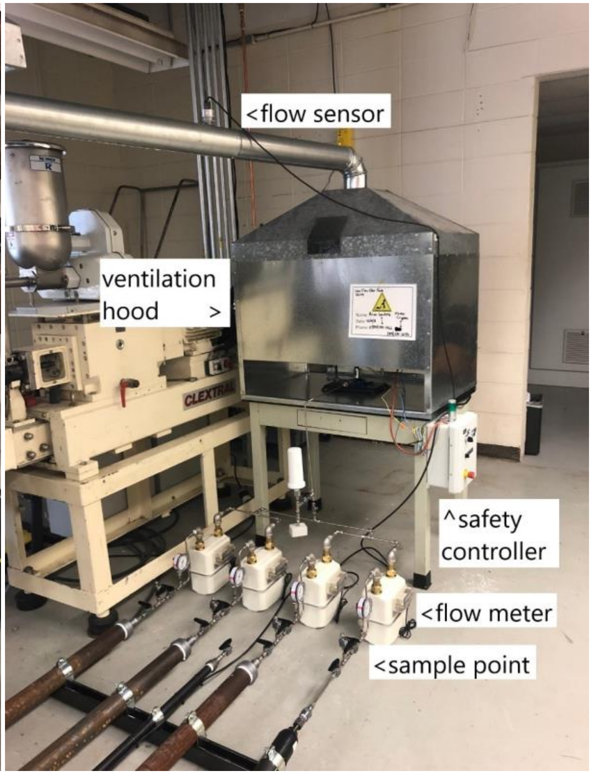
- To overcome odorant fade, operators generally add supplemental odorant.
- In conjunction with this, natural gas flow rates can be increased to purge more gas.
- Unfortunately, this option cannot be utilized in situations where the flow can be very low to non-existent, especially in summer months.

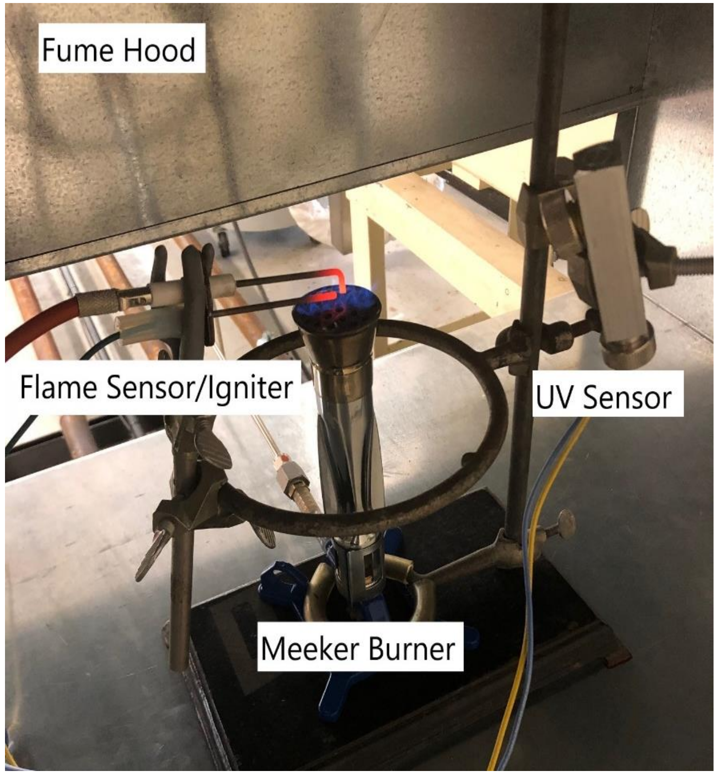
432 Park Avenue, NYC is the third tallest building in the United States, and the tallest residential building in the world

One Mitigation Option is an Internal Coating

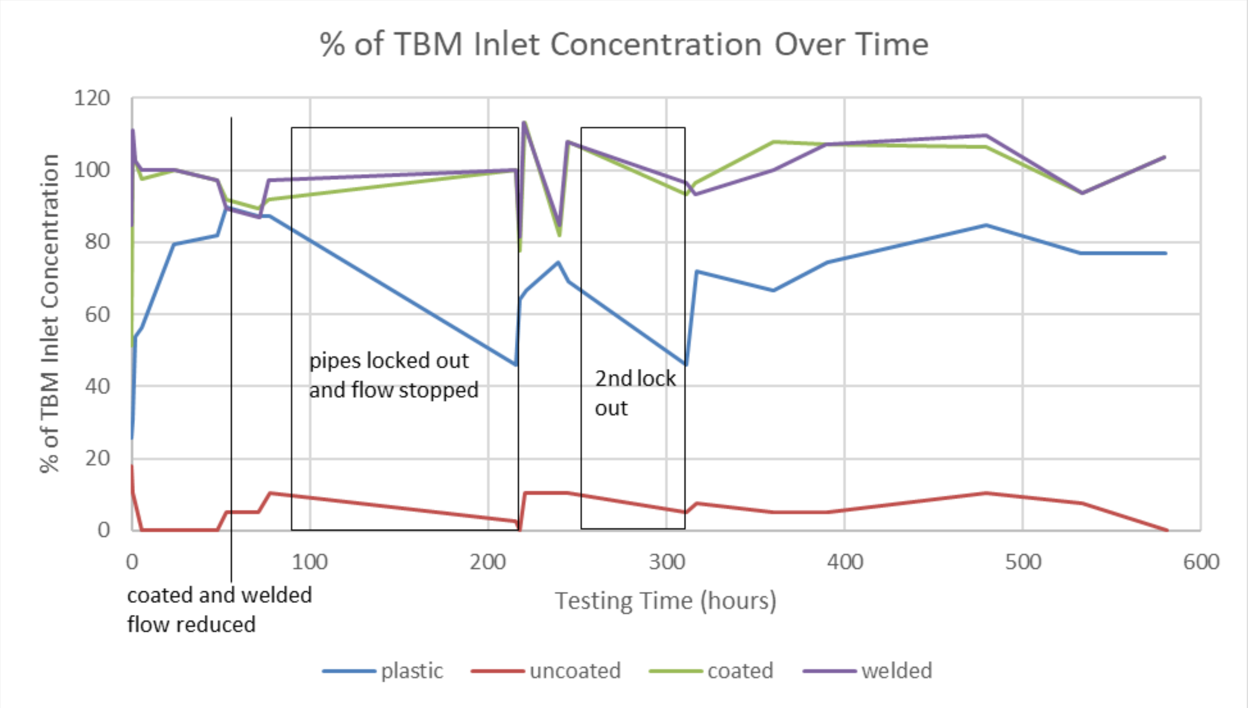
- Induron Pipeliner SG coated steel pipe, 2 inch diameter, recommended by PSEG
- Coating is a polyamidoamine epoxy material

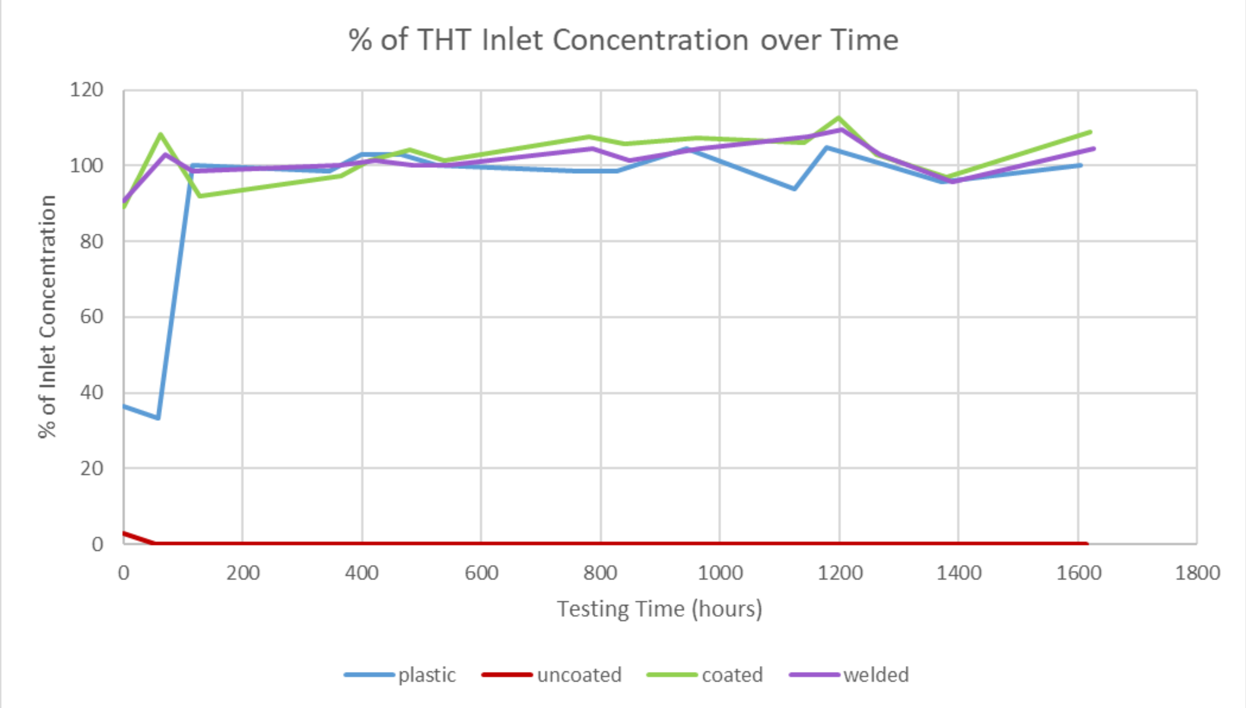






Coating Study - Results

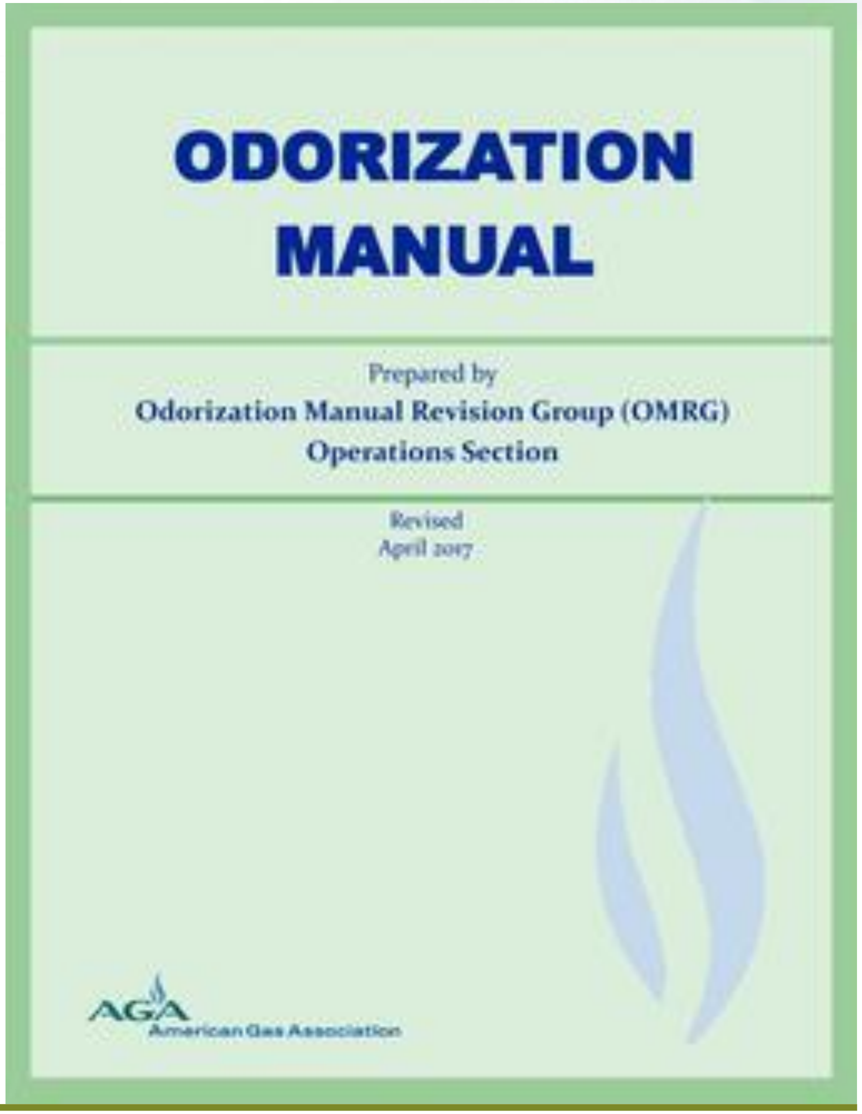




- Coated steel pipe will remediate odor fade problems under low flow conditions (0.25 ft^3/hour). The coating material is unaffected by welding.
- When pipe must be inserted where concerns of odor fade are present, this coating could be considered as a solution.

What is a Good Resource for Odorization Questions?

- Take a look at the AGA Odorization Manual
- Updated in 2017 (last edition was 2000)
  - Went from 66 pages to 172 pages
- The manual includes expanded and new sections on odorization system design, results of odor fade and masking research, pipeline conditioning, gas odor assurance testing, safety and environmental aspects and operator training.



Any Questions?

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