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Executive Summary

Odorants used in the gas industry in North America all contain sulfur, carbon, and hydrogen and belong to a category of chemicals known as organosulfurs. The most common odorants used are alkyl mercaptans such as t-butyl mercaptan, alkyl sulfides such as dimethyl sulfide (added to lower the freezing point of the mixture), and tetrahydrothiophene (a cyclic odorant). This project was designed to investigate causes of odor fade in natural gas distribution systems.

A preliminary literature survey reviewed the availability of current and historical data. It concluded that the primary causes of odorant fading include: 1) surface interactions of odorants with different pipe materials, 2) scrubbing or dissolution by condensates or cleaning fluids, 3) chemical reaction/oxidation of odorant with other components in the gas stream, and 4) other system state variables.

Thermodynamic prescreening was one tool used to look at the possible reactions involving more common blend stock odorants. In addition to forming (mainly) disulfides and iron sulfides, mercaptans might also decompose or react with trace gas processing constituents (e.g., methanol).

To obtain specific detailed data from project stakeholders, two survey questionnaires were designed. The first survey form focused on pipeline odor fade events and the second on pre-conditioning (pickling) and supplemental odorization. Five surveys were received back. In general, the odor fade survey results indicated that:

- Most odor fade events were reported to have been prompted by weak sniff test results and most respondents reported performing follow-up quantitative analyses.
- No instances of solvent odors were reported.
- Two odor fade events were reported with plastic (PE) pipe, the others with steel pipe.
- Ambient temperature ranged from 20-90°F
- All events involved a single source of natural gas.
- No pipe cleaning was mentioned as having been employed by any of the respondents
- Odorants involved were t-butyl mercaptan mixtures with either dimethyl sulfide, i-propyl mercaptan, or tetrahydrothiophene; no odorizer operational issues were noted.
- Supplementary odorant injection was employed to increase odorant levels by all but one of the respondents.

Laboratory batch or “static” testing was conducted to obtain data regarding odorant loss under various selected conditions of gas composition, temperature, and pipe system material. The tests were designed to simulate a “locked-in” condition. As t-butyl mercaptan is the organosulfur compound most commonly used in natural gas odorants, it was selected for initial testing. Tetrahydrothiophene was tested to a lesser extent.

Containers used for testing odorant loss consisted of sections of plastic and steel pipes and two inerted stainless steel sampling cylinders. Analysis of sulfur compounds was by gas chromatography with a pulsed flame photometric detector.

The trace constituents water, oxygen, methanol, monoethanolamine, and hexanes were added to the inerted test vessels at concentrations up to the maximum values found in available gas quality data. Monoethanolamine was selected as a surrogate amine compound representing volatile amine compounds used for natural gas treatment and as a constituent in hydrofracturing fluids.

Tests on the steel and plastic vessels were limited to studying odorant loss and developing Arrhenius rate constants and parameters.

Results confirm expectations that the variable that most impacted t-butyl mercaptan concentration in the gas phase was the presence of rust on the pipe surface. The concentration of t-butyl mercaptan in a steel pipe fades very rapidly until active sites are quenched.

Testing with liquid t-butyl mercaptan injected to quench a used rusty pipe also showed a rapid loss of t-butyl mercaptan. By the fourth injection cycle, the initial rate of t-butyl mercaptan decrease had slowed to less than a fourth of the initial average rate, confirming that the active sites were gradually being depleted.

This confirmed field data from four case studies of pre-odorization/pickling. The field data indicate that by using the technique of injection of highly odorized gas, (TBM or TBM/IPM and MES blends), 0.2 to 0.4 mL/ft^2 of odorant addition was required to achieve full conditioning. Nearly double the odorant addition rate was required when using a continuous liquid addition technique. The odorant addition rate was significantly lower (0.05 mL/ft^2) when using THT as the odorant, due to its known lower reactivity.

Testing with trace contaminants in the inerted reactor were reported with a statistical evaluation of the data. There was no odorant fading in the presence of 1000 ppmv oxygen, 19 ppmv methanol, 1000 ppmv hexanes, and 141 ppmv water. There was evidence of odor fade in the presence of 152 ppmv methanol and ~60 and 21 ppmv monoethanolamine (MEA).

Field data was used to obtain some correlations with system variables. An increase in gas pressure appeared to induce increased absorption and adsorption, and concurrently an increase in oxidation from surface rust and induced odor fade. Pipe diameter also showed some correlation as would be expected, with larger pipes required more odorant to be added. This supports the concept of using internal surface area to determine initial odorant addition.

Ansys Fluent software modeling was used with literature and two sets of GTI laboratory-generated data. Odorant consumption rates based on literature data were less than anticipated. In the case of the baseline model against the literature data, the data was shown to be incomplete from the perspective of assessing the pressure-dependency of odorant consumption reactions. In addition, it was skewed in the treatment of second-order temperature effects, in that the odorant consumption had an inverse relation to temperature. This relationship later prompted the added temperature dependency in the Arrhenius rate expression.

The second model used GTI data generated at two different temperatures. This dataset was an improvement as it eliminated the inverse temperature effect seem with the literature data. However, this model over estimated odorant loss.

Therefore, a third iteration of modeling was performed on new lab data obtained from four different temperatures, as opposed to just two temperatures as used in the first set of lab data. Also included was a study on how the presence of water impacted the reaction of TBM in bare steel pipe. This new multi-step mechanism was not modeled as zeroth order, but rather was modeled as a series of first order reactions. Another important aspect of this revised modeling was the shift from the use of a thin volumetric reaction zone to surface chemistry on the interior wall itself, requiring a shift in both how parameters are treated and which submodels were deployed.

Overall the following observations can be made:

- TBM loss in plastic pipe was higher at higher temperatures. The rate of loss was also higher in the hotter specimens.

- THT loss was higher in the hotter specimens. The rate of loss was slightly higher in the hotter specimens.
- TBM is more reactive with the steel pipe material than with the plastic pipe material.
- Steel pipe exhibited loss of both TBM and THT. Increasing the temperature increased odorant loss, and increased the rate of loss.
- Rusty steel pipe showed the greatest TBM odorant loss.
- Bare steel pipe also showed high TBM loss. When water was introduced into the steel reactor, the rate of loss increased further. Water by itself had no effect (as seen in the inerted reactor tests), but had a significant effect when iron was present.
- TBM adsorption and desorption reactions have slightly larger rates than the reaction itself and adsorption may be favored over desorption for the temperature range considered.
- Initial modeling of the 1-step versus multi-step reaction mechanism showed the multi-step mechanism to be more robust.

Modeling using field data was originally intended to be accomplished through a series of physical tests on pipeline segments and/or systems. The original option as described in the proposal involved piggy backing on an already operating line at one of the stakeholder companies.

However, discussions with project stakeholders suggested that there were many issues regarding the field testing of long lengths of piggy backed pipe initially proposed to be performed at company sites. These issues include the extensive amount of time, work and cost that would be required for this type of testing. None of the other project participants want to piggy back any pipe onto their existing pipelines.

The best solution was to do odorant analysis during an actual natural gas pipeline installation and/or conditioning project. Economic factors delayed many significant new construction projects for the companies contacted. Unfortunately, as the project concluded, only two companies were able to supply any useful field data. As a result, conclusions are limited. In the field simulations, the THT odorant loss was significantly overestimated. The TBM odorant loss was also overestimated, although to a lesser extent.

The information gained in this project was used to prepare a suggested revision to Chapter 7 of the current edition of the AGA Odorization Manual, last revised in 2000. It was announced at an AGA workshop held in Denver on November 19-20, 2013 that a team was being formed to begin revisions to the manual in 2014. GTI intends to be involved in this process and the information developed in this project will guide the odor fade section.

Recommendations were also made for further testing.

Introduction

Because methane by itself is odorless, odorants have been added to natural gas streams in the United States ever since the 1937 Texas school explosion. The requirement that gas in certain classes of natural gas transmission and distribution pipelines be odorized (or contain a natural odorant) is documented in 49 CFR 192.625.[1,2] The purpose of the odorant is for people to quickly detect a leak if it is present. However, using only the sense of smell to detect natural gas can present a problem under certain conditions where the perceived odor has diminished.

The loss or change of odor in natural gas is usually attributed to two different causes, odor fade and odor masking. These two issues are distinct. Odor fade can be defined as the loss of odorant by physical or chemical processes occurring inside the pipeline. These processes can include: (a) Adsorption or other surface interactions of odorant with pipe materials, (b) Scrubbing/dissolution by condensate or cleaning liquids, or (c) Chemical reaction/oxidation of odorant with other components, e.g., trace constituents in the gas stream and carryover of chemicals from wellhead conditioning or gas processing etc. Inside the pipe, odor fade is influenced by: (1) Materials of construction, (2) Gas quality and composition, (3) Odorant type, and, (4) System variables.

Odor masking is the change in perception of the characteristic gassy smell of odorants present in natural gas. Odor masking occurs in the human nose and is still poorly understood. It is a distinct/separate issue requiring a separate research effort. This project focuses on odor fade.

To overcome odor 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. Unfortunately, typical supplemental odorant injection and control is based on a non-technical approach. Anecdotal information is the basis of most current guidelines. This "Rule of Thumb Approach" is employed where some pipeline operators use an odorizing “cookbook” or “one size fits all” recipe with mixed results. The usage and information regarding supplemental odorization varies with company policy, or may not be formally defined at all. The American Gas Association (AGA) Odorization Manual (~50 page document) does highlight some potential fade causes (~ 2 pages of information), but it does not provide specific guidance or solutions to manage the odor fade problem.

Loss of odorant effectiveness in natural gas is not a new phenomenon. It has lately become a high-profile issue for the natural gas industry due to recent gas explosions and increased litigation due to perceived odor fade. The US Chemical Safety Board recently investigated five cases[3] in which the odor of natural gas was called into question: a 2009 explosion at the ConAgra Slim Jim Plant in Garner North Carolina, killing four, severely burning three, and sending 67 people to the hospital; a 2008 explosion at a Hilton Hotel under construction in San Diego, California that injured fourteen people; an explosion at a hotel in Cheyenne, Wyoming, in 2007 severely burning two plumbers; a 2005 school explosion in Porterville, California, burning two plumbers; and a 1999 explosion at a Ford power plant in Dearborn, Michigan, killing six, injuring 38, and causing $1 billion in property losses.

These incidences led to the conclusion that there is a clear need to better manage odor fade issues and to investigate and address the primary causes of odorant fading in natural gas systems.

The benefits of quantifying and providing a practical, simple operator guide to manage odor fade issues are all linked to the PHMSA (Pipeline and Hazardous Materials Safety Administration) mission of safety and environmental protection. Specifically the information from this project will aid in 1) minimizing the number of odorant-related incidents and associated harm; 2) improving public safety and regulatory compliance, including Distribution Integrity Management Program compliance; 3) promoting acceptability of renewables by quantifying the impact of trace constituents (if any) on odorant within gas supplies; 4) assuring continuity of safe pipeline operations by proactively addressing the loss of experience and expertise due to the retirement of odorant subject matter experts; and 5) reducing operating costs for odorant programs by optimizing supplemental odorant injection rates.

The project was divided into several tasks to accomplish its goals. The first task was a review of odor fade information from industry sources, standard documents, research reports, and publications in scientific journals, providing an overview of odor fade issues. An overview of odor fade issues related to propane was also performed. The literature review information was used to identify and define the known variables affecting odor fade. The next step was to simplify the model and to reduce the number of initial variables using thermodynamic prescreening, prior testing, literature, and operator experience. The goal was to account for the majority of the variables that result in significant odor fade, while not oversimplifying too much. Chemical stability testing was performed using t-butyl mercaptan (TBM) in inerted reactors. Temperature stability was tested using TBM and tetrahydrothiophene (THT) in steel and plastic reactors. All of this data was used to generate a preliminary odor fade model using ANSYS® Fluent®, a fluid flow simulation software package. Some limited field data was used with the model equations to determine what modifications to the model might be needed. The final task pulled together the knowledge and information gained through the previous tasks and drafted a preliminary "Practical Pipeline Operator Guide" to overcome odor fade issues based on the information obtained.

Literature Review of Odor Fade Issues

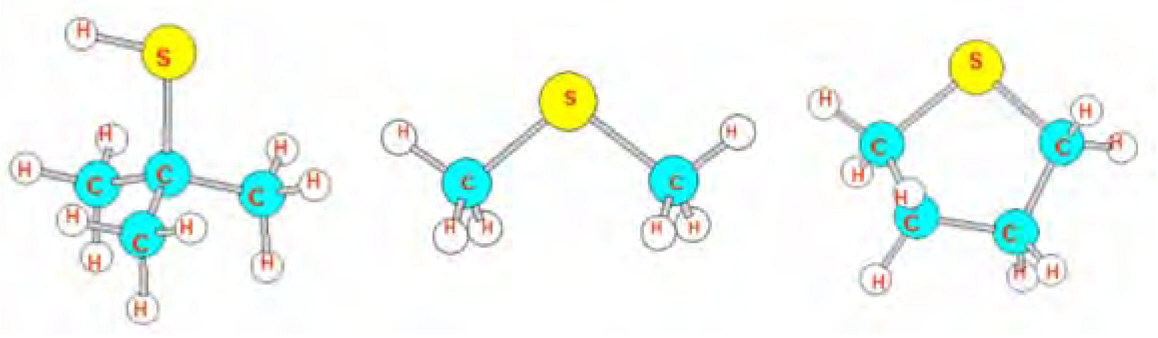
Task 1 of this project includes a comprehensive review of odor fade information from industry sources, standard documents, research reports, and publications in scientific journals, providing an overview of odor fade issues.[4-86] The literature review also provides information about odorant fade knowledge gaps. The literature review helped to identify those key variables considered for the construction of the odor fade model(s) in later tasks.

Initial conclusions on the primary causes of odorant fading in natural gas systems include: 1) surface interactions of odorants with different pipe materials, 2) scrubbing or dissolution by condensates or cleaning fluids, 3) chemical reaction/oxidation of odorant with other components in the gas stream, and 4) other system state variables.

Types of Odorant used in North America

Odorants used in the gas industry in North America all contain sulfur, carbon, and hydrogen and belong to a category of chemicals known as organosulfurs. As depicted in Figure 1, there are three general classes of organosulfur compounds:

1. Alkyl mercaptans or thiols such as t-butyl mercaptan (TBM), contain chains of CH2 groups (linear and branched) terminating in an S-H group. The structure is similar to alcohols, except a sulfur atom is substituted for an oxygen atom (hence the thiol name similarity to alcohol). The relative reactivity of the mercaptan odorants depends on the length and position of the alkyl group; the longer and more highly substituted the alkyl group, the less reactive the molecule.
2. Alkyl sulfides or thioethers, such as dimethyl sulfide (DMS), contain chains of CH2 groups linked by a sulfur atom, similar to the oxygen atom in an ether molecule. They are resistant to oxidation but do not have the odor impact of the mercaptans. They are used primarily to lower the freezing point of the odorant mixture.
3. Cyclic odorants, the most common being tetrahydrothiophene (THT). THT is more thermally and chemically stable than both alkyl mercaptans and alkyl sulfides. It is used alone, or in combination with TBM, as a natural gas odorant.



TBM DMS THT

Figure 1. Molecular Structure of Various Types of Sulfur Odorant Compounds

While industry occasionally uses a single odorant chemical, blends are more typically used to achieve the best compromise between resistance to fade, odor impact and cost.

Tertiary butyl mercaptan (TBM) is the organosulfur compound most commonly used in natural gas odorants today. It has a low odor threshold, good soil penetration, and the highest resistance to oxidation of the mercaptans due to its branched structure. These characteristics make TBM chemically attractive. Its relatively high freezing point (34°F), however, requires it to be blended with other components to prevent freezing in odorization equipment in cold weather.

TBM is commonly blended with an alkyl sulfide such as dimethyl sulfide (DMS) or methyl ethyl sulfide (MES). These sulfide compounds will usually not oxidize in the pipeline. TBM is also blended with THT, which has the best resistance to oxidation. However, THT has low odor impact and poor soil penetrability. THT-TBM is the most expensive blend stock and will require increased odorant injection rates to achieve the same odor impact associated with mercaptan or mercaptan-sulfide blends. TBM is reported to show lower adsorption to PE-pipe than THT.[11]

Different mercaptans are also blended to make a commercial odorant, usually TBM with isopropyl mercaptan (IPM) and n-propyl mercaptan (NPM). The latter two compounds have much lower freezing points, but they are more susceptible to oxidation. Non-branched mercaptans like NPM are much more prone to oxidation, followed by branched mercaptans like IPM and TBM.

As direct odorant injection equipment can be used on small systems as well as large system, their use has helped eliminate many odorization problems, and has also reduced the number of blends used.

Roberts and Kelley report in a 1992 odorization symposium paper that odorant selection is important.[68] Their paper states “The major role in keeping gas odorant concentrations at acceptable levels should be in the pressure at which the system is maintained. A lower gas pressure should result in higher flows in the distribution system which should minimize odorization problems. If the problem is severe, a switch to a higher vapor pressure odorant, one containing larger quantities of isopropyl mercaptan, might help. This should be considered to be a fairly drastic solution to the problem.”

Many companies odorize at rates between 0.5 and 1.0 pounds per MMSCF although this does vary widely. Anecdotal information suggests injection rates do not vary in the summer when gas volumes flowing through the pipeline are reduced. Those companies that do make changes, base the changes on flowing gas proportionalities: as gas flow rates are reduced during summer months and gas becomes stagnant in the pipe, odorant effectiveness is lowered.

Early Research into Odorant Fade

The phenomenon of odorant loss (i.e., odor fade) from both natural gas and LPG gas streams has been observed within the industry for the last 60 years.[70] Usually the reports and information are anecdotal and not well documented.

AGA Report PM-34[54] contains early research (1961) into odorant compound chemistry. Among the report’s conclusions, it finds through thermodynamic calculations and reports in the literature of the time that:

- Catalytic oxidation of mercaptan to disulfide is highly probable in the presence of O_2.
- Reformation of mercaptans to thioethers and hydrogen sulfide (or with iron present to iron sulfide) is probable.
- Reaction between mercaptans and metallic iron or copper is probable in hot lines and less probable in cold lines.
- Decomposition of mercaptans to olefins is improbable.
- Oxidation of mercaptans to sulfonic acids is favored but not generally observed except in the presence of a strong oxidizing agent as an initiator.
- Tetrahydrothiophene is amenable to oxidation but the reaction is difficult to initiate.

AGA initiated an investigation at the Institute of Gas Technology (IGT, now GTI) in March 1962 to study the kinetics of various reactions leading to odor fading. Project PB-48 was terminated in December 1965 with a final report and dissemination of findings to industry.[6,7,32,33,34,38] Although this investigation was limited to the laboratory, experimental tests were conducted under simulated distribution pipeline conditions. Primary emphasis in this study was directed toward obtaining a quantitative representation of laboratory experimental results that could be directly translated to predict behavior in pipelines.

The Consumers Product Safety Commission (CPSC) focused attention on the problem of odorant fade in liquefied petroleum (LP) gas through a series of studies and symposia that were conducted in the mid-1980's. One study[9] looked at LP gas odorant reactions with gas storage cylinders and masonry surfaces.

Anecdotal Information on Odor Fading

Over 75% of natural gas companies have reported experiencing odorant reduction or odor fade in newly installed steel transmission and distribution lines upstream of the meter.[84] Odor fading in previously installed piping was reported by 32% of the companies in another survey.[18] The occurrence of odor fade was also reported for newly installed plastic pipe albeit at a lower response rate than for steel pipe.[4,61]

Many companies have formal monitoring procedures in place for steel pipe, but fewer have procedures in place for monitoring odor fade in plastic pipe. Those companies that monitor also perform localized supplemental odorization as a mitigation measure upstream of the meter.

Odorant Adsorption and Absorption Reactions

Odorant fade can occur when the odorant molecules adhere or adsorb onto the surface of the pipe. This prevents the odorant from travelling down the pipeline with the natural gas that was originally odorized. Until equilibrium is reached, the odorant levels will continue to be reduced and odorized gas will not remain odorized.

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. The 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.

The odor fade phenomena cannot be attributed to adsorption alone. An early report by Johnson[33] concluded that physical adsorption of mercaptans on pipeline surfaces could not account for a significant fraction of the amounts of various odorants that disappeared in pipelines, and that odorant alteration was due primarily to chemical transformation of one odorant species into another species with lesser or greater odor levels. However, adsorption is the first step in any oxidation mechanism (as discussed below), since it usually occurs on the oxide surface of the pipeline.

Absorption, the filling of pores in a solid, or dissolution into a liquid, is different a process from *adsorption*. 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. Not only can odorants be physically absorbed into plastic pipe materials (possibly during pickling),[39,40,83] they can also be absorbed into hydrocarbon condensates or other liquids 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.

Odorants Reactions with Rust and Mill Scale Inside New Steel Pipes

Steel mills produce metal sheets destined for pipeline construction by rolling red hot iron or steel billets in rolling mills.[16] During this high temperature process mill scale is formed on the outer surfaces. Mill scale is a bluish black form of iron oxide commonly called magnetite (Fe_3O_4) and containing iron in both the +2 and +3 valence state. It is found on all hot-rolled steel products unless they are processed in a protective atmosphere or descaled (e.g., for galvanizing). At first the mill scale strongly adheres to the steel surface and, because it is electrochemically cathodic to steel, it offers protection from atmospheric corrosion.

Once cooled, steel pipe is produced from these metal sheets by rolling and welding the sheets into a circular form. The procedure causes breaks in the mill scale coating, allowing accelerated corrosion of the exposed steel by oxidation with atmospheric oxygen and moisture, ultimately inducing surface rust to occur. This rust consists of hydrated iron(III) oxide ($Fe_2O_3 \cdot nH_2O$) and iron(III) oxide-hydroxide (($FeO(OH)$ and $Fe(OH)_3$),[6,8,9,37,76,77,78] all having a characteristic reddish orange color.

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 as shown in the reactions below.[16,17,18,29,30,57,67,70,81]

$$2\ RSH + 3\ Fe_2O_3 \cdot nH_2O \rightarrow RSSR + 2\ Fe_3O_4 + (n+1)\ H_2O$$

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

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

R stands for any aliphatic hydrocarbon chain.

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. The odor fade phenomenon is more pronounced in new steel pipe of large diameters and longer lengths because of the greater surface area and thus greater amount of rusty active sites. Odorized gas entering the newly installed line will be gradually stripped of mercaptan as it travels through the pipe and can potentially be left with no remaining odorant when it reaches the end user. Until all of the active sites are used up (or passivated) the reactions will continue.[8] Older pipe will remain passivated unless the surface is refreshed through a pigging operation or other pipeline maintenance operation.

One project stakeholder has shared information that they have had issues with different pipeline material manufacturers; it is the same type of pipe (same specifications) but the pipe comes from different suppliers. This could be due to slightly different steel grain structures from different steel producers, and may be dependent on how the pipe was milled, and how the mill scale or rust formed.

The mechanism and kinetics of the mercaptan oxidation reaction in ambient temperature systems are still not fully understood. Experiments initiated in 1962[6,7,32,33,34] applied to gas distribution systems found that the rate of mercaptan conversion to disulfides was dependent on several factors: mercaptan and disulfide feed concentrations, oxygen, gas flow rate, solids surface area, time and type of mercaptan. Although mathematical expressions were developed to describe these effects on mercaptan conversion rates, no steady-state oxidation reaction was achieved of any four of the mercaptans used in this study. A number of other experimental studies[9,46,54,55,76,77,78] of mercaptan oxidation have since been conducted, although no similar correlations were developed.

Other favorable reactions forming other than disulfides can be postulated, such as for ethyl mercaptan:

$2\ C_2H_6S\ (g) + FeO \rightarrow n\text{-}C_4H_{10}\ (g) + FeS_2 + H_2O(g)$ $\log K_0=27.3$

$2\ C_2H_6S\ (g) + FeO \rightarrow n\text{-}C_4H_{10}S\ (g) + FeS + H_2O\ (g)$ $\log K_0=10.9$

These reactions demonstrate a positive standard-state equilibrium constant (K_0). However, in most cases, it appears that the reactions to form the disulfides are more rapid.[23]

Other Possible Chemical Reactions Involving Mercaptan Odorants

As can be seen from the chemical reactions shown below, low molecular weight mercaptans might also form iron sulfide in pipelines as indicated by the highly positive K_0 values.

Tertiary butylmercatan

$C_4H_{10}S\ (g) + Fe \rightarrow n\text{-}C_4H_{10}\ (g) + FeS$ $\log K_0=21.2$

Isopropyl mercaptan

$C_3H_8S\ (g) + Fe \rightarrow C_3H_8\ (g) + FeS$ $\log K_0=21.5$

Normal butylmercaptan

$C_4H_{10}S\ (g) + Fe \rightarrow n\text{-}C_4H_{10}\ (g) + FeS$ $\log K_0=22.8$

Tetrahydrothiophene

$C_4H_8S\ (g) + Fe \rightarrow i\text{-}C_4H_8\ (g) + FeS$ $\log K_0=15.8$

$C_4H_8S\ (g) + Fe \rightarrow n\text{-}C_4H_8\ (g) + FeS$ $\log K_0=13.4$

Dimethyl sulfide

$C_2H_6S\ (g) + Fe \rightarrow C_2H_6\ (g) + FeS$ $\log K_0=24.9$

Methyl ethyl sulfide

$C_3H_8S\ (g) + Fe \rightarrow C_3H_8\ (g) + FeS$ $\log K_0=24.0$

The interaction of plastic pipe and odorant has also been experimentally studied.[76] Gas odorized with TBM left in polyethylene (PE) pipe at relatively low pressure for three weeks showed no measurable loss in odor intensity when checked by an odorometer. In the same study a minimal effect was noted in vapor phase odorant contact with polyvinyl chloride (PVC).

Effects of Pipeline Conditions

Temperature: Raising the gas temperature can have opposing effects. In the adsorption process, a higher temperature will drive off the adsorbed molecule. But, any odorant molecule in contact with the surface would have a greater chance of undergoing oxidation from surface rust due to the temperature effect on the rate of oxidation (the reaction rate increases at higher temperatures). Lowering the temperature increases the probability of both absorption and adsorption, and gives oxidation from surface rust a greater chance to occur due to increased residence time despite the reduced rate of oxidation.[53]

Pressure: An increase in gas pressure will induce increased absorption and adsorption, and concurrently an increase in oxidation from surface rust and odor fade. Changing the gas line pressure can also impact on the flow rate if all other conditions remain the same. Laminar flows will decrease with lower pressure, turbulent flows (possibly due to oversized pipe) may increase with lower pressure, if the flow goes from a turbulent to a laminar regime.

Flow rate: Odorant fade can occur under low flow conditions because diffusion of the odorant molecules is more probable with the increased residence time. Increasing the gas flow rate decreases the residence time and the likelihood of odor fade lessens. One study[54] recommended maintaining a minimum gas velocity of 10 ft/sec in the pipeline to prevent odor fading due to stagnation.

Surface area: As the pipeline moves toward the end user, the diameter of the pipe tends to decrease. This lowers the gas volume- to- interior- surface- area ratio and increases the potential surface interaction. The more surface area available, the more physical processes such as adsorption and absorption will occur. This is true for both the bare metal and any entrained iron oxide coating. Physically, the powdery surface area of the iron oxides is greater than the bare metal. The greater the surface area the greater is the affinity to adsorb odorant.

The actual pipeline location can contribute to the challenge. Elevation changes along a pipeline may cause localized “low spots” that could accumulate condensates, water, rust or pipeline dust, causing areas where gas odorant can encounter very favorable conditions for odor fade. This makes a new pipeline pickling or seasoning process much more difficult and lengthy.

Effect of Varying Gas Composition

Natural gas and other fuel gases are complex mixtures of hydrocarbons and other gases that do not contribute to the BTU content, depending on the geologic or renewable source. Odorant fade will occur with varying gas compositions. This problem will continue as more non-traditional sources of gas are introduced into the distribution system such as landfill gas and other renewables, coal seam gas, and shale gas. Of specific concern, aside from major hydrocarbon content, are trace components such as benzene, toluene, ethyl benzene and xylenes (BTEX), formaldehyde, nitrogen oxides, naturally occurring odorants such as methyl mercaptan (MM) and ethyl mercaptan (EM), and corrosion inhibitors.

Raw landfill gas can contain oxygenates, such as alcohols, acids and esters as well as olefinic compounds, all of which can act as masking agents or possibly react with odorants if not removed during gas upgrading. It is often hard to tell if a problem is related to odor fade or odor masking. As an example, one instance[13] was reported by a utility where gas from a processing plant was being odorized with a mixture of t-butyl mercaptan and propyl mercaptan isomers at appropriate concentrations (as verified by analysis) yet a large fraction of the gas stream had no detectable odor.

Condensates

Table 1 shows some compositional data for various wellhead natural gases produced in the US.[28] The compositions have considerable variability and the impact on the presence of hydrocarbon condensates is substantial. Were all of the condensable components of the examples shown in Table 1 to liquefy, the calculated volumes of condensate that would be produced would be the liquid volumes shown in Table 2. Gas stream #1, a lean gas, would produce no condensate. Gas stream #2, which is not atypical, would deposit a layer of condensate between 0.2-2.0 mils thick along a one mile stretch of 30-inch diameter pipe.

Table 1. Example Well Head Gas Stream Compositions, Percent of Total

	Gas 1	Gas 2	Gas 3	Gas 4	Gas 5
Methane	96.7	88.9	77.8	71.2	39.7
Ethane	0.4	5.4	9.3	12.4	15.5
Propane	0.1	2.2	6.0	7.4	23.5
n-butane	BDL	0.7	2.1	2.7	9.6
i-butane	Trace	0.2	0.8	1.3	6.2
n-pentane	Trace	0.2	0.5	0.8	1.8
i-pentane	Trace	0.2	0.5	1.4	2.3
Cyclopentane	Trace	0.1	0.1	0.3	0.2
Hexane+	Trace	BDL	0.2	0.9	0.8
Nitrogen	2.7	BDL	2.5	0.7	0.3
Oxygen	BDL	BDL	BDL	BDL	Trace
Argon	Trace	Trace	Trace	BDL	BDL
H_2S	BDL	BDL	BDL	BDL	BDL
CO_2	Trace	Trace	0.1	0.9	0.1
He	0.08	0.1	0.04	0.01	Trace
Heating Value, BTU/SCF	989	1,111	1,265	1,421	2,046

Table 2. Condensate Formed per MMSCF @ 60°F at Various Pressures from Gas Streams in Table 1

	Condensate, gallon/MMCF			
	50 psig	100 psig	200 psig	300 psig
Gas 1	0	0	0	0
Gas 2	40	58	70	92
Gas 3	92	134	214	317
Gas 4	681	943	1,517	2,104
Gas 5	1,337	4,931	13,703	21,463

If a hydrocarbon condensate is present, it can dissolve the organosulfur odorant. The propensity for dissolution of a gas into a liquid is known as the distribution coefficient or $K_{d,}$ the ratio of the vapor phase concentration to the liquid phase concentration. For the mercaptans, the larger the molecule, the smaller is K_d, meaning more molecules will be in the liquid phase. The implication for odorant loss is that once an odorant is absorbed into a liquid hydrocarbon, there will be a significant drop in odorant gas phase concentration that is not recoverable. If a less hydrocarbon-rich gas stream enters the pipeline, the condensate will begin to evaporate. Because the odorant does not evaporate at the same rate as the condensate, the possibility exists that the gas may ultimately become over odorized.

Condensation can occur during other gas processing practices. In transmission lines, gas is often compressed to increase flow rates. Upon compression, condensation may occur. Upon expansion when going from a transmission line to a distribution line, cooling of the gas stream will occur, also possibly creating condensates. Oil fogging of new pipelines also takes place. One report notes that when fogging rates are greater than one gallon per MMSCF, the loss of odor is in direct proportion to the fogging rate.[56] The same paper reports that methanol scrubbed a considerable amount of odorant from the gas stream. Methanol is occasionally used to prevent pipeline freezing. While it is more of an odor masking issue, the presence of heavier hydrocarbons in the gas stream can overpower the smell of any odorant. An instrumental analysis would show the presence of odorant, but it would be undetectable by a sniff test.

Clearly, some knowledge of the actual composition of the gas stream and pipeline conditions must be available to predict whether a particular gas sample is prone to condensation and odor fading.

Propane-Air Peak Shaving

Propane-air peak shaving can impact odorant in two different ways. Primarily, the presence of oxygen will directly promote oxidation of the odorant molecule. If a pipeline previously held gas from peak shaving operations, catalytic oxidation could still occur by (overall) reaction of the mercaptan odorant with adsorbed or absorbed (in the case of plastic pipe) molecular oxygen:

$$2\ RSH + \tfrac{1}{2}\ O_2 \rightarrow RSSR + H_2O$$

Although this reaction is slow in air in the vapor phase, it can be accelerated under a variety of actual/real world conditions.

Simulated pipeline fading tests, which involved passing gas odorized with TBM through a column packed with a highly active iron oxide, were conducted at oxygen levels of 0.25% and 2.5%. The results of these tests indicated no significant effect of oxygen concentration on the breakthrough time (indicator of extent of adsorption) of the TBM.[77] It was also shown in two other investigations[19,46] comparing the rate of reaction of EM, IPM and TBM in the gas phase in a number of different metal containers that the mercaptan oxidation is dependent on the nature of the oxidized surface rather than the oxygen content of the gaseous reactant mixture.

Other Trace Components

It has been reported[38] that naturally occurring mercaptan odorants of lower molecular weight (MM and EM) may induce loss of higher molecular weight mercaptan odorants (such as TBM) by catalyzing the oxidation reaction. Another study[8], however, found no evidence of TBM conversion by the lower molecular weight ethyl mercaptan used in the experiments and apparently contradicts the above earlier findings. In any case, the prevailing opinion in the literature appears to be that gases containing naturally occurring mercaptans if blended with TBM-odorized gas generally need supplemental odorization[28,29,36,57,61,62,66,67,72,76,80,81] (usually with THT unless the gas is susceptible to condensate formation).

Hydrogen sulfide is also very reactive with mercaptan odorants. It is more reactive with TBM than MM and EM as mentioned previously. Mercury vapor will also react with mercaptans.

$$2\ RSH + Hg \rightarrow RS\text{-}Hg\text{-}SR + H_2$$

Other reactions of mercaptans with potential trace constituents include a reaction that occurs in the presence of air and nitrogen oxides yielding a sulfonic anhydride. Adding moisture yields a sulfonic acid. The nitrogen oxide is not consumed but is required as a catalyst.

Common Ways Gas Companies Combat Odor Fade

Often a pre-odorizing step is required to completely saturate and deactivate new gas pipe. This process is known as pickling. There are three basic methods to accomplish pickling:

1. Injection of an already highly odorized gas.
2. Adding a bulk amount of odorant directly into the pipeline (or slugging) and allowing the pipe to remain stagnant with no flowing gas.
3. Continuous injection of odorant directly into the flowing gas stream.

While the practice of pickling or slugging new gas lines is common, there is little in the literature in terms of the quantity of odorant that might be required to deactivate the line. Five recent case studies of pre-odorization[14,21,22,26,27,41,42,45] summarize the various scenarios followed to attain properly odorized gas, and provide some information on the type of odorant employed, the response of the line, the amount of odorant required to saturate the line, and the odorant dosages and measurements. The results of two of the above case studies were also discussed in a recent review article.[30]

A 1965[20] reference describes using two mixtures for conditioning new pipe: A mixture of a low-vapor-pressure oil containing a rust inhibitor and a mixture of kerosene (80%), mercaptans (10%) and cyclic odorants (10%). Also, old gas mains were conditioned using supplemental odorization rates of 0.5-1.5 pounds per 1,000,000 cubic foot of gas for up to three years before the by-pass odorizers were removed. A 1959[85] reference describes coating the mains with epoxy resin, a one-shot oil-odorant injection or spraying of an oil-odorant mixture (11% odorant, 89% oil).

An early study[53] and more recent studies[23,74] identify other possible methods for negating the adsorption and reaction of mercaptan odorants by the iron oxide scale. These methods included: coating, passivating or poisoning the inside surface of the pipe, adding a surrogate substance to the gas in addition to the mercaptans, and installation of plastic sleeves or introduction of a thin polymer film on the inside surface of the pipe. The intent of some of these studies was to coat/inactivate both new unoxidized and oxidized surfaces.

Odor Fade Issues Related to the Use of Propane and Propane Pipelines

Natural gas is not the only fuel transported through pipelines that is required by law to be odorized. Propane gas or LP gas (liquefied petroleum gas) is also required to be odorized in accordance with 49 CFR 173.315(b)(1) and National Fire Protection Association (NFPA) Standard 58 paragraph 1-4.1. Propane is a colorless paraffin hydrocarbon with the chemical formula C_3H_8 and a molecular weight of around 44. LP gas is a generic term referring to liquefiable hydrocarbons. The most common LP gas contains mostly propane but also lesser amounts of other hydrocarbons such as butane and propylene. This contrasts with natural gas, which is predominately methane, CH_4, with a molecular weight of around 16. Various other hydrocarbons are also present in natural gas in decreasing concentrations.

Propane is denser than natural gas (methane) and has a higher heating value. At typical ambient conditions propane is a gas, however when it is compressed or if the temperature falls, it becomes a liquid. This is the state that propane is normally stored at, it is 270 times more compact; it is energy dense and cheaper to transport.

The liquefaction process for LP gases was discovered in 1912 when Snelling discovered that certain gases could be changed into liquids and stored under pressure.[87] The LP gas industry started after the initial development of the natural gas industry and before WWI when these liquefiable hydrocarbons were found during routine gas processing. LP gas is now produced as a by-product of both the petroleum and natural gas industries. It is used as a petrochemical feedstock and to satisfy residential, agricultural, and commercial energy needs.[88]

Propane and LP gas are commonly odorized with ethyl mercaptan (EM). Ethyl mercaptan was one of the first odorants used in the fuel gas industry, back in the 1880s when town gas or manufactured gas (i.e. manufactured from coal and oil) was the fuel gas of choice. The concern at that time was the presence of poisonous CO in the gas mixture. As the natural gas industry began to grow, natural gas started replacing town gas in many applications. Because natural gas can contain naturally occurring odorants that can result in a detectable odor and the CO concern was removed, natural gas at that time was often not odorized. The 1937 New London High School explosion in New London Texas changed that when it prompted states to adopt regulations that standardized natural gas odorization for pipeline gas for consumer use.

Fuel gases were odorized by a variety of synthetic odorants up until the early 1950s, but by 1960, almost all fuel gas was odorized by one or more odorant compounds:

1. Alkyl mercaptans or thiols contain chains of CH2 groups (linear and branched) terminating in an S-H group. The structure is similar to alcohols, except a sulfur atom is substituted for an oxygen atom (hence the thiol name similarity to alcohol). The relative reactivity of the mercaptan odorants depends on the length and position of the alkyl group, the longer and more highly substituted the alkyl group is, the less reactive the molecule is.
2. Alkyl sulfides or thioethers contain chains of CH2 groups linked by a sulfur atom, similar to the oxygen in an ether. They are resistant to oxidation but do not have the odor impact of the mercaptans. They are used primarily to lower the freezing point of the odorant mixture.
3. Cyclic odorants, the most common being tetrahydrothiophene (THT). THT is more thermally and chemically stable than both alkyl mercaptans or alkyl sulfides.

While the natural gas industry made several modifications to the odorant added to its gas, the propane industry decided to keep EM as their main odorant compound. The primary reason is that EM works well with liquid propane. This is important because while propane is used as a fuel in a gaseous state, it is generally distributed as a liquid. In order for propane to be used as a fuel the liquefied propane is vaporized. For proper odorization this vaporization process must carry the odorant along.

When a compound is dissolved in a condensable liquid with a considerable vapor pressure, like propane, it is not equally distributed between the liquid and gaseous phases. The compound's distribution coefficient is a factor that describes the ease by which the compound is released into the gas phase. A larger value means more of the compound will transfer to the vapor phase. The distribution coefficients for LP gas and several common odorants used in the LP industry are listed in Table 3.[92,93,94] Also listed in Table 3 are each compound's vapor pressure and molecular weight. Again a larger vapor pressure is preferred. As seen, in general the equilibrium vapor pressures for closely related compounds follow the molecular weights of the compounds. Ethyl mercaptan has the largest distribution coefficient and highest vapor pressure. Based on this data DMS would also appear to be a potential odorant for LP gas, but its olfactory impact in LP gas applications is much less than EM.

Table 3. Distribution Coefficient in LP Gas and Equilibrium Vapor Pressures for Sulfur Odorants at 60°F

Compound	Distribution Coefficient in LP Gas at 60°F	Molecular Weight	Vapor Pressure, atm
ethyl mercaptan	0.252	62.1	0.478
i-propyl mercaptan	0.124	76.2	0.244
t-butyl mercaptan	0.071	90.2	0.158
dimethyl sulfide	0.235	62.1	0.437
tetrahydrothiophene	0.007 (est.)	88.2	0.014

Some thought has been given to searching for an odorant blend to use similar to the standard practice for the natural gas industry. As Table 3 suggests, the varying distribution coefficients of potential odorants make it very difficult to formulate a blend of chemicals that would provide a consistent odor to the gas.

The vaporization process also has a temperature correlation. Vapor pressure increases with temperature, so an odorant will tend to stay in the liquid phase during cold temperature months. The relationship between vapor pressure and temperature for pure components is described by the Antoine equation:

$$\log\left(P^{*}\right) = A - \frac{B}{T + C}$$

Where P^{*} is the vapor pressure, T is the absolute temperature, and A, B, and C are empirically derived constants. Table 4 shows the A, B, and C constants for EM and compares them to propane and methane (natural gas).[92,93,94]

As can be seen, the EM constants are more similar to propane than they are to methane. It should be noted that the temperature ranges given in this table for propane and methane are lower than for EM, because they exist entirely in the gas phase above the maximum temperature at atmospheric pressure.

Table 4. Antoine Equation Parameters for Ethyl Mercaptan, Propane, and Methane

Compound	Temperature Range, °K	A, bar	B, bar	C, °K
Ethyl mercaptan	274-339	4.07696	1,084.53	-41.77
Propane	166-231	4.01158	834.26	-22.76
Methane	110-190	4.22061	516.69	11.22

These parameters do point out one drawback to propane odorization. Since propane is usually odorized in large reservoir storage tanks before being distributed, the EM levels in the liquid phase become stronger as the propane levels in the tank decrease. As Table 3 indicates, only about 25% of the potentially available odorant is capable of being in the gas phase. Since the EM molecule does not volatilize at the same rate as propane (propane is more volatile than EM), there is a constant increase in concentration of odorant in the liquid phase as the product is dispensed. This leads to ever increasing EM concentrations in the gas stream as the propane storage tank levels decrease.

This high vaporization also offers an advantage with maintenance and cleaning. Operators will often open valves to help with the desorption process when cleaning tanks or lines. This allows the gas to vent to atmospheric pressure, as opposed to staying at pipeline pressure. The pressure differential is sometimes enough to free the EM from inner pipe wall surfaces were it may tend to adsorb.[94]

Odorant fade in metal pipe and containers used in the propane and LP gas industry can occur through several different mechanisms. The following information is summarized from information previously reported. (This task was added to the project at DOT/PHMSA's specific request, and was originally submitted as a separate task report. Some information reported herein is duplicated from the original literature survey task.)

- Adsorption (gas phase)
- Absorption
- Oxidation
- Pipeline Conditions

<u>Adsorption:</u> Gas phase adsorption is the process by which a molecule or particle is physically attracted 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. The 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.

Gas phase odorant molecules can be adsorbed onto metal surfaces. This physical process prevents the odorant from travelling down the pipeline with gas that was originally odorized. Until equilibrium is reached, the odorant levels will continue to be reduced and odorized gas will not remain odorized. While mostly a gas phase phenomenon, adsorption can also occur in liquids. This is the basis for certain forms of liquid chromatography.

<u>Absorption</u>: Absorption, the filling of pores in a solid, is different a process from *adsorption*. 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. This mostly occurs with plastic piping and is not common with metal piping.

Oxidation: Steel mills produce metal sheets destined for pipeline and container construction by rolling red hot iron or steel billets in rolling mills. During this high temperature process, mill scale is formed on the outer surfaces. Mill scale is a bluish black form of iron oxide commonly called magnetite (Fe_3O_4) and containing iron in both the +2 and +3 valence state. It is found on all hot-rolled steel products unless they are processed in a protective atmosphere or descaled (e.g., for galvanizing). At first the mill scale strongly adheres to the steel surface and because it is electrochemically cathodic to steel it offers protection from atmospheric corrosion.

Once cooled, steel pipe is produced from these metal sheets by rolling and welding the sheets into a circular form. Gas cylinders have separate specific requirements for their fabrication, including a heat treatment step. These procedures can cause breaks in the mill scale coating and it may spall off, allowing accelerated corrosion of the exposed steel. The oxidation of the bare steel with atmospheric oxygen and moisture can ultimately induce surface rust to occur. This rust consists of hydrated iron(III) oxide ($Fe_2O_3 \cdot nH_2O$) and iron(III) oxide-hydroxide (($FeO(OH)$ and $Fe(OH)_3$), all having a characteristic reddish orange color.

As a result of the production process, the interior walls of new steel pipe and containers can contain very reactive iron oxide compounds, which will react with ethyl mercaptan to form less odorous diethyl disulfide, magnetite, and water as shown in the reactions below.

$$2\ CH_3CH_2SH + 3\ Fe_2O_3 \cdot nH_2O \rightarrow CH_3CH_2SS\ CH_2CH_3 + 2\ Fe_3O_4 + (n+1)\ H_2O$$

$$2\ CH_3CH_2SH + 6\ FeO(OH) \rightarrow CH_3CH_2SS\ CH_2CH_3 + 2\ Fe_3O_4 + 4\ H_2O$$

$$2\ CH_3CH_2SH + 6\ Fe(OH)_3 \rightarrow CH_3CH_2SS\ CH_2CH_3 + 2\ Fe_3O_4 + 10\ H_2O$$

These reactions are all thermodynamically favored in terms of both enthalpy and free energy, and will occur spontaneously. The equivalent reaction with Fe_3O_4 is not thermodynamically favored and the presence of Fe_3O_4 serves to passivate exposed surfaces.

Not only does diethyl disulfide possess lower olfactory impact than mercaptans, it has a much lower vapor pressure so will be more likely to adsorb on metal surfaces. The odor fade phenomenon is more pronounced in new steel pipe and containers of large diameters and longer lengths because of the greater surface area and thus greater amount of rusty active sites. Odorized gas or liquid coming into contact with surfaces containing these reactive iron oxides can be gradually stripped of mercaptan and can potentially be left with no remaining odorant when it reaches the end user. Until all of the active sites are used up (or passivated) the reactions will continue.

Mercaptan compounds have different reactivities, depending on their chemical structure and branching. The oxidation of EM occurs much more easily than oxidation of other odorants. Table 5 lists the relative reactivity of mercaptan odorant compounds used in the natural gas and LP gas industries. The commonly used TBM odorant is set at a value of one and used as a reference point. Ethyl mercaptan (highlighted) is near the bottom of the list, with respect to exhibiting a low reactivity. Despite this, the industry has concluded that no single odorant or odorant blend would be superior to EM.

Table 5. Relative Reactivity of Mercaptans

Compound	Relative Reactivity
t-butyl mercaptan	1.00 (Reference)
i-propyl mercaptan	1.36
sec-butyl mercaptan	2.0
n-butyl mercaptan	91.0
n-propyl mercaptan	98.3
n-amyl mercaptan	123
ethyl mercaptan	**227**
methyl mercaptan	1,820
hydrogen sulfide	5,000+

<u>Pipeline Conditions</u>: Raising the gas temperature can have opposing effects. In the adsorption process, a higher temperature will drive off the adsorbed molecules. But, any odorant molecule in contact with the surface would have a greater chance of undergoing oxidation from surface rust due to the temperature effect on the rate of oxidation (the reaction rate increases at higher temperatures). Lowering the temperature increases the probability of both absorption and adsorption, and gives oxidation from surface rust a greater chance to occur due to increased residence time despite the reduced rate of oxidation.

An increase in gas pressure will induce increased absorption and adsorption, and concurrently an increase in oxidation from surface rust and result in odor fade. Changing the gas line pressure can also impact on the flow rate if all other conditions remain the same. Laminar flows will decrease with lower pressure, turbulent flows (possibly due to oversized pipe) may increase with lower pressure, if the flow goes from a turbulent to a laminar regime.

Odorant fade can occur under low flow conditions because diffusion of the odorant molecules is more probable with the increased residence time. Increasing the gas flow rate decreases the residence time and the likelihood of odor fade lessens.

Internal surface area is also a consideration. Smaller pipelines and vessels have smaller diameters and less surface area. This can lower the volume- to- interior- surface- area ratio and increase potential surface interactions such as adsorption and absorption.

The composition of the metal surface is important. Copper pipelines exist, and these are not compatible with ethyl mercaptan (or any mercaptan). Over time, mercaptans will also degrade the zinc in brass fittings that are commonly used in copper pipelines. This phenomenon is known as “dezincification”, and will corrode the metal and cause leaks.

<u>Varying Gas Compositions</u>: This factor is more prevalent in the natural gas industry. Many new sources of natural gas are coming on line and compositions vary according to their geologic or renewable source.

Odor fade in liquid propane storage vessels is a well-documented phenomenon. In October of 1987 the United States Consumer Product Safety Commission addressed the issue in an official Memorandum. The Memorandum cites a 1986 report from Frontier Technical Associates reviewing the overall safety of residential LP gas systems,[95] and a 1987 Arthur D. Little report evaluating the effects of rust and masonry surfaces.[9] Many others have studied odor fade in LP gas steel cylinders.[44,50,73,89] All of these reports noted in detail the tendency of ethyl mercaptan to react with rust on the inside of propane storage tanks, resulting in odor fade. This concern ultimately prompted the LP gas industry to routinely offer consumer warning information regarding the potential for odor fade in older or rusted propane tanks.

The Arthur D. Little report focused on EM odorized propane gas in used and new 100 pound steel cylinders. Rust was visually present and characterized by x-ray diffraction as mostly hematite and maghemite, different crystalline forms of Fe_2O_3 or iron III oxide. A Parr reaction chamber was selected to simulate the propane tank and coated with a simulated rust layer. The reactor was filled with liquid propane odorized at the level of 1.5 lbs EM per 10,000 gallons of propane. In just a week, levels were found below the National Fire Protection Association (NFPA) recommended level of 1.0 lbs. ethyl mercaptan per 10,000 gallons of propane. Most of the oxidation took place within a few hours. The researchers discovered that the primary oxidation product was diethyl sulfide. Repeated filling of the reactor exhibited a decrease in oxidation rate, showing that it is better to top off tanks frequently to help prevent the oxidation of ethyl mercaptan. The other case studies have confirmed the data trend.

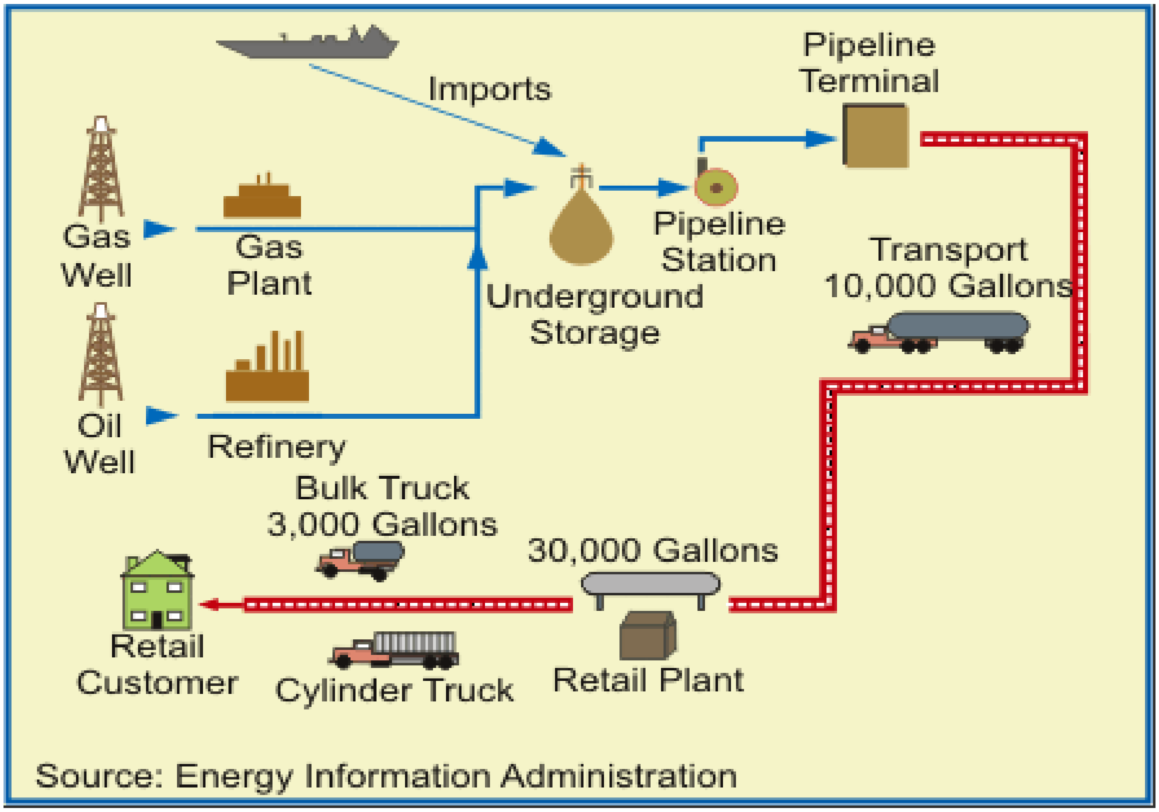
There are ways to minimize odor fade, such as passivation of pipelines and adding an inert coating. The latter option is not very applicable, due to its high cost. The NFPA and National Propane Gas Association (NPGA) have several codes and bulletins addressing odorant fade in LP gas. These include:

- NFPA 58 Liquefied Petroleum Gas Code (Storage and Handling Liquefied Petroleum Gas)
- NPGA Bulletin No. 133 “Purging New Containers”
- NPGA Bulletin No. 202 “After Accident Procedure”

<u>Other Considerations for Propane</u>

Propane has a much higher relative density than natural gas. At 60˚F and atmospheric pressure, propane has a relative density of 1.51 as opposed to the 0.60 relative density of natural gas. Since the relative density is a ratio of the gas density to air, propane is heavier than air while natural gas is lighter than air. This property may cause propane to be undetected by the nose even though it is odorized, due to propane staying low to the ground. This also renders the traditional barholing technique that the natural gas industry uses for ground leak detection ineffective. Propane will stay low to the ground, and will not rise up to be detected like natural gas.

Propane is typically distributed as liquefied LP gas via underground pipelines to distribution terminals from natural gas processing plants and oil refineries. Information from the NPGA indicate that there are about 70,000 miles of propane and LP gas pipelines in the US.[96] Propane storage facilities can consist of pressurized geologic salt dome storage caverns and depleted mines, along with above ground tanks. These are generally located near major production and transportation hubs in Kansas and Texas. Smaller regional storage hubs are in New York, Ohio Illinois, Michigan, Minnesota and Louisiana. Other modes of distribution include rail tank cars, highway bulk transports, local delivery trucks, and water-based barges and tankers. Figure 2 shows a diagram from the U.S. Energy Information Administration (EIA) outlining the process.[88]



Source: Energy Information Administration

Figure 2. Propane Production and Distribution System

The U.S. Department of Transportation Pipeline and Hazardous Materials Safety Administration (DOT/PHMSA) also offers data that details pipeline operator information including operators with hazardous liquid, gas transmission, and/or gas gathering pipelines who have submitted one or more PHMSA-required annual reports for the 2006-2012 time period.[97] They state that smaller gas distribution assets are not currently included in these reports. The data includes basic mileage, incident, inspection, and enforcement information covering the last five years.

An examination of the available data lists 53 companies that operate LP liquid or propane gas pipelines in the US in 30 different states. Texas, Louisiana, and Kansas comprise nearly 75% of the LP liquid pipeline miles. States that report statistics on propane pipelines include Kansas, Iowa, Illinois, Texas, and Indiana, in decreasing order of mileage.

While the U.S. propane distribution system is not very large (approximately 600 miles), it serves a variety of end use customers. Pressures range from 100 psi at the storage reservoirs to 2 psi in distribution lines, and down to inches of water column pressure at residential service lines. Some companies that own propane pipelines or distribute propane gas are listed in Table 6. These include major propane suppliers as well as some local distribution companies (LDCs) with service areas that do not have natural gas distribution lines, often due to their rural nature. These areas are mostly isolated homes, trailer parks, and some commercial strip malls.

Table 6. Companies That Own Propane Pipelines or Who Distribute Propane

Company	Active US States
Inergy Propane, LLC	California
Amerigas Propane LP	California, Arizona
Oneok NGL Pipeline LP	Kansas, Illinois and Iowa
Suburban Propane Partners LP	California, Mississippi, New Jersey
Buckeye Partners LP	Illinois
Dow Chemical	Texas
Southern California Edison	California (Catalina Island)
Florida Public Utilities	Florida
Chesapeake Utilities	Delmarva Peninsula

Often these distribution lines are served by a central fuel storage area, or cluster tank systems with multiple fuel storage tanks. The advantage is that individual storage tanks are not required at every user's site. Metered gas service is provided via a service line tapped into the distribution main in the same manner as distributed natural gas.

Identify and Define Variables that Affect Odor Fade

The information obtained in the literature survey was used to further define those variables leading to odor fade. These include interactions with pipeline surfaces, interactions with other gas components, odorant type, system conditions, and others as discovered as necessary. The variable list was further prioritized in the following task in order to help simplify the model, and reduce the amount of validation testing.

A. Potential Gas/Condensate Composition Parameters to Input into the Model

1) Major Gas Components:
    a) Hydrocarbon breakdown (lean vs. rich; straight chain vs. aromatic; etc.)
    b) Gas processing constituents (amines, methanol, glycol, etc.)
    c) Propane/air peak shaving
    d) Minor Constituents (CO_2, H_2S, H_2O, O_2, Etc.)
2) Minor Gas Components:
    a) Odorant Type (mercaptans, blends, sulfides, etc.)
    b) Trace Constituents (e.g., from shale gas, coal seam, landfill, wastewater, dairy/biogas, wellhead condition, etc.)
3) Condensate/Solids Composition (scrubbing issues):
    a) Liquid water drop out
    b) Liquid hydrocarbon drop out
    c) Solid/particulate matter (corrosion product, sulfides/disulfides, oxides, scrapings, etc.)
    d) Cleaning and biocide agents

B. Potential Pipe System Material Parameters to Input into the Model

1) Pipe Material:
    a) Plastic Pipe (MDPE, HDPE, PA, etc.).
    b) Iron Based Pipe (bare steel, flow-coated steel, Cast Iron, Ductile Iron, Rimmed vs. HSLA, etc.)
    c) Copper Based Tubing
    d) Lined Pipe (Thermoset binders)
2) Age or Prior Pickling of Pipe
    a) New Pipe (polymer or metal)
    b) Old/Exposed Pipe (polymer or metal)

C. Potential Operating System Variables

1) Pressure (and variations)
2) Temperature (and variations)
3) Flow:
    a) Static (no flow) vs. Dynamic (flow)
    b) Velocity (and variations)
    c) Regime (laminar/stratified vs. turbulent); single vs. multiple injections
    d) Direction (unidirectional vs. bidirectional)
4) Odorant
    a) Injection Type: batch and/or continuous
    b) Injection Site: single or multiple
5) Length of pipe runs
6) Diameter (surface area) to volume ratio of system
7) Pipe geometry (multiple branching and termination points

Prioritizing and Weighing of Variables

To simplify the model, and reduce the amount of validation testing, the number of model variables needed to be reduced. Based on thermodynamic prescreening, prior testing, literature, and operator experience the most critical variables were selected to develop a simplified model with a reduced set of inputs. This task assumed that the variables could be reduced to the variables that affect fade the most.

A hot topic that has been mentioned by several stakeholders and other industry contacts is the effects of hydraulic fracturing chemicals on odor fade. Some of the chemicals are volatile enough that the question arises if they are present in the gas phase. While their presence in pipeline natural gas is unknown, we wanted to investigate their impact. Table 7 lists some volatile hydraulic fracturing chemicals that are found in publically available tables.[98-99] Selected fracturing chemicals or their surrogates were considered for static laboratory testing in Task 4.

Table 7. Selected Volatile Chemicals Used in Hydraulic Fracturing

1,2,4-Trimethylbenzene
1,3,5-Trimethylbenzene
2,2-Dibromo-3-Nitrilopropionamide
2.2-Dibromo-3-Nitrilopropionamide (DBNPA)
2-Butoxyethanol
2-Ethylhexanol
2-Methyl-4-isothiazolin-3-one
5-Chloro-2-methyl-4-isothiazotin-3-one
Acetic Acid
Acetic Anhydride
Alphatic Acid
Methanol
Butanol
Dazomet
Diethylbenzene
Dodecylbenzene sulfonic acid
Dodecylbenzenesulfonate isopropanolamine
Ethoxylated alcohol (surfactants)
Ethoxylated octylphenol
Ethylbenzene
Ethylene glycol
Ethylene glycol monobutyl ether
Ethylhexanol
Formaldehyde
Glutaraldehyde
Isopropanol
Monoethanolamine
Naphthalene
Nitrilotriacetamide
Polyethoxylated alkanol (1)
Polyethylene glycol mixture
Polyglycol ether mineral spirits
Prop-2-yn-1-ol (propargyl alcohol)
Propylene
Tetramethylammonium chloride
Toluene
Xylene

Thermodynamic prescreening was one tool used to look at the interactions. Table 8 summarizes the thermodynamic data obtained for possible reactions involving more common blend stock odorants using the HSC Chemistry Chemical Reaction and Equilibrium Software program. The current version of this program's main database contains thermochemical data of more than 25,000 species. As shown in the table, there is the potential for a significant number of reactions to occur in an odorized pipeline gas system. In addition to forming (mainly) disulfides and iron sulfides, mercaptans might also decompose (such as by reaction 49 catalyst unknown) or react with trace gas processing constituents (e.g., methanol reaction 26). Potential reactions are indicated by a positive standard state equilibrium constant (logK) value.

Vapor pressure data (Table 9) is also useful in screening the volatile chemicals used in hydraulic fracturing. The highlighted chemicals have significant vapor pressure (e.g., >10 mm Hg) at room temperature.

Table 8. Thermodynamic Data for Possible Reactions Involving Blend Stock Odorants

Reaction #	R 1	Ph	R 2	Ph	R 3	P 1	Ph	P 2	Ph	P 3	Ph	Reaction	delta H, kcal/mole	delta S, cal/mole	delta G, kcal/mole	K	log K
1	DMS	g	Fe	c		FeS	c	ethane	g			C2H6S(g)+Fe↔C2H6(g)+FeS	-35.57	-5.56	-33.91	7.26E+24	24.86
2	DMS	g	O_2(g)	c		ethylene glycol (EGg)	g	S_8	g			C2H6S(g)+O2(g)↔C2H6O2(EGLg)+1/8S8(g)	-81.05	-27.08	-72.98	3.16E+53	53.50
3	DMS	g	O_2(g)	c		ethylene glycol (EGl)	l	S_8	g			C2H6S(g)+O2(g)↔C2H6O2(EGLl)+1/8S8(g)	-96.73	-64.54	-77.49	6.42E+56	56.81
4	EM	g	$Fe(OH)_3$	c		diethyl disulfide (DEDg)	g	Fe_3O_4	c	H_2O	l	2C2H6S(EETg)+6Fe(OH)3↔C4H10S2(DEDg)+2Fe3O4+10H2O(l)	-14.61	43.45	-27.56	1.60E+20	20.20
5	EM	l	$Fe(OH)_3$	c		diethyl disulfide (DEDl)	l	Fe_3O_4	c	H_2O	l	2C2H6S(EETl)+6Fe(OH)3↔C4H10S2(DEDl)+2Fe3O4+10H2O(l)	-12.06	60.13	-29.99	9.63E+21	21.98
6	EM	g	$Fe(OH)_3$	c		diethyl disulfide (DEDg)	g	Fe_3O_4	g	H_2O	g	2C2H6S(EETg)+6Fe(OH)3↔C4H10S2(DEDg)+2Fe3O4+10H2O(g)	90.57	327.59	-7.10	1.61E+05	5.21
7	EM	g	Fe_2O_3	c		diethyl disulfide (DEDg)	g	Fe_3O_4	c	H_2O	l	2C2H6S(EETg)+3Fe2O3↔C4H10S2(DEDg)+2Fe3O4+H2O(l)	-8.52	-19.11	-2.82	1.17E+02	2.07
8	EM	g	Fe_2O_3	c		diethyl disulfide (DEDg)	g	Fe_3O_4	c	H_2O	g	2C2H6S(EETg)+3Fe2O3↔C4H10S2(DEDg)+2Fe3O4+H2O(g)	2.00	9.31	-0.78	3.70E+00	0.57
9	EM	g	Fe_2O_3	c		diethyl disulfide (DED)	l	Fe_3O_4	c	H_2O	l	2C2H6S(EETg)+3Fe2O3↔C4H10S2(DEDl)+2Fe3O4+H2O(l)	-19.13	-44.21	-5.95	2.31E+04	4.36
10	EM	g	Fe_2O_3	c		diethyl disulfide (DEDl)	l	Fe_3O_4	c	H_2O	g	2C2H6S(EETg)+3Fe2O3↔C4H10S2(DEDl)+2Fe3O4+H2O(g)	-8.62	-15.79	-3.91	7.32E+02	2.87
11	EM	l	Fe_2O_3	c		diethyl disulfide (DEDl)	l	Fe_3O_4	c	H_2O	l	2C2H6S(EETl)+3Fe2O3↔C4H10S2(DEDl)+2Fe3O4+H2O(l)	-5.97	-2.43	-5.25	7.04E+03	3.85
12	EM	l	Fe_2O_3	c		diethyl disulfide (DEDg)	g	Fe_3O_4	c	H_2O	l	2C2H6S(EETl)+3Fe2O3↔C4H10S2(DEDg)+2Fe3O4+H2O(l)	4.64	22.67	-2.12	3.56E+01	1.55
13	EM	l	Fe_2O_3	c		diethyl disulfide (DEDg)	g	Fe_3O_4	c	H_2O	g	2C2H6S(EETl)+3Fe2O3↔C4H10S2(DEDg)+2Fe3O4+H2O(g)	15.16	51.08	-0.07	1.13E+00	0.05
14	EM	l	Fe_3O_4	c		diethyl disulfide (DEDg)	g	FeO	c	H_2O	l	2C2H6S(EETl)+Fe3O4↔C4H10S2(DEDg)+3FeO+H2O(l)	24.80	21.84	18.29	3.92E-14	-13.41
15	EM	g	Fe_3O_4	c		diethyl disulfide (DEDg)	g	FeO	c	H_2O	g	2C2H6S(EETg)+Fe3O4↔C4H10S2(DEDg)+3FeO+H2O(g)	22.16	8.48	19.63	4.07E-15	-14.39
16	EM	g	Fe_3O_4	c		diethyl disulfide (DEDg)	g	FeO	c	H_2O	l	2C2H6S(EETg)+Fe3O4↔C4H10S2(DEDg)+3FeO+H2O(l)	11.64	-19.94	17.58	1.29E-13	-12.89
17	EM	l	Fe_3O_4	c		diethyl disulfide (DEDl)	l	FeO	c	H_2O	l	2C2H6S(EETl)+Fe3O4↔C4H10S2(DEDl)+3FeO+H2O(l)	14.18	-3.26	15.16	7.75E-12	-11.11
18	EM	g	FeO	c		diethyl disulfide (DEDg)	g	Fe	c	H_2O	l	2C2H6S(EETg)+FeO↔C4H10S2(DEDg)+Fe+H2O(l)	-0.14	-33.54	9.86	5.94E-08	-7.23
19	EM	g	FeO	c		diethyl disulfide (DEDg)	g	Fe	c	H_2O	g	2C2H6S(EETg)+FeO↔C4H10S2(DEDg)+Fe+H2O(g)	10.37	-5.13	11.90	1.88E-09	-8.73
20	EM	g	FeO	c		butyl mercaptan (BETg)	g	FeS	c	H_2O	g	2C2H6S(EETg)+FeO↔C4H10S(1BETg)+FeS+H2O(g)	-16.90	-6.68	-14.91	8.54E+10	10.93
21	EM	g	FeO	c		n-butane (NBAg)	g	FeS_2	c	H_2O	g	2C2H6S(EETg)+FeO↔C4H10(NBAg)+FeS2+H2O(g)	-42.41	-24.15	-35.20	6.42E+25	25.81
22	EM	g	FeO	c		n-butane (NBAg)	g	FeS_2	c	H_2O	l	2C2H6S(EETg)+FeO↔C4H10(NBAg)+FeS2+H2O(l)	-221.43	-219.94	-155.85	2.03E+27	27.31
23	EM	l	FeO	c		n-butane (Bl)	l	FeS_2	c	H_2O	l	2C2H6S(EETl)+FeO↔C4H10(Bl)+FeS2+H2O(l)	-44.87	-29.76	-36.00	2.46E+26	26.39
24	EM	g	FeO(OH)	c		diethyl disulfide (DEDg)	g	Fe_3O_4	c	H_2O	l	2C2H6S(EETg)+6FeO*OH↔C4H10S2(DEDg)+2Fe3O4+4H2O(l)	-0.51	7.10	-2.63	8.41E+01	1.93
25	EM	g	FeO(OH)	c		diethyl disulfide (DEDg)	g	Fe_3O_4	c	H_2O	g	2C2H6S(EETg)+6FeO*OH↔C4H10S2(DEDg)+2Fe3O4+4H2O(g)	41.56	120.75	5.56	8.44E-05	-4.07
26	EM	l	methanol(l)	c		propane (PPEg)	g	S_8	g	H_2O	g	CH3OH(l)+C2H6S(EETl)↔1/8S8(g)+H2O(l)+C3H8(PPEg)	-15.30	13.63	-19.36	1.55E+14	14.19
27	EM	g	O_2	g		diethyl disulfide (DEDg)	g	H_2O	g			2C2H6S(EETg)+0.5O2(g)↔C4H10S2(DEDg)+H2O(g)	-53.51	-22.40	-46.83	2.13E+34	34.33
28	EM	l	O_2	g		diethyl disulfide (DEDl)	l	H_2O	l			2C2H6S(EETl)+0.5O2(g)↔C4H10S2(DEDl)+H2O(l)	-61.48	-34.14	-51.30	4.04E+37	37.61
29	EM	g	O_2	g		ethylene glycol (EGLl)	l	S	s			2C2H6S(EETg)+0.5O2(g)↔C2H6O2(EGLl)+S(c)	-97.55	-72.63	-75.89	4.33E+55	55.64
30	EM	g	O_2	g		ethylene glycol (EGLg)	g	S	s			2C2H6S(EETg)+0.5O2(g)↔C2H6O2(EGLg)+S(c)	-81.87	-35.17	-71.38	2.13E+52	52.33
31	IPM	g	Fe	c		propane (PPEg)	g	FeS	c			C3H8S(2PATg)+Fe↔C3H8(PPEg)+FeS	-30.90	-5.21	-29.35	3.26E+21	21.51
32	MES	g	Fe	c		propane (PPEg)	g	FeS	c			C3H8S(EMSg)+Fe↔C3H8(PPEg)+FeS	-34.86	-7.09	-32.75	1.01E+24	24.01
33	NBM	g	Fe	c		n-butane (NBAg)	g	FeS	c			C4H10S(1BETg)+Fe↔C4H10(NBAg)+FeS	-33.40	-7.82	-31.07	5.99E+22	22.78
34	NBM	l	Fe	c		n-butane (Bl)	l	FeS	c			C4H10S(1BTl)+Fe↔C4H10(Bl)+FeS	-29.50	-2.75	-28.68	1.06E+21	21.02
35	TBM	g	Fe	c		isobutane (2MPAg)	g	FeS	c			C4H10S(2M2Pg)+Fe↔C4H10(2MPg)+FeS	-30.62	-3.07	-29.70	5.94E+21	21.77
36	TBM	g	Fe	c		n-butane (NBAg)	g	FeS	c			C4H10S(2M2Pg)+Fe↔C4H10(NBAg)+FeS	-28.57	1.33	-28.96	1.70E+21	21.23
37	TBM	g	$Fe(OH)_3$	c		dibutyl disulfide (DBDg)	g	Fe_3O_4	c	H_2O	g	2C4H10S(2M2Pg)+6Fe(OH)3↔C8H18S2(DBDg)+2Fe3O4+10H2O(g)	100.25	345.89	-2.88	1.29E+02	2.11
38	TBM	l	$Fe(OH)_3$	c		dibutyl disulfide (DBDl)	g	Fe_3O_4	c	H_2O	g	2C4H10S(2M2Pl)+6Fe(OH)3↔C8H18S2(DBDl)+2Fe3O4+10H2O(l)	-5.62	72.61	-27.27	9.82E+19	19.99
39	TBM	l	Fe_2O_3	c		dibutyl disulfide (DBDl)	l	Fe_3O_4	c	H_2O	l	2C4H10S(2M2Pl)+3Fe2O3↔C8H18S2(DBDl)+2Fe3O4+H2O(l)	0.47	10.05	-2.53	7.18E+01	1.86
40	TBM	g	Fe_2O_3	c		dibutyl disulfide (DBDg)	g	Fe_3O_4	c	H_2O	g	2C4H10S(2M2Pg)+3Fe2O3↔C8H18S2(DBDg)+2Fe3O4+H2O(g)	-3.81	-3.95	-2.64	8.58E+01	1.93
41	TBM	g	Fe_2O_3	c		dibutyl disulfide (DBDl)	l	Fe_3O_4	c	H_2O	g	2C4H10S(2M2Pg)+3Fe2O3↔C8H18S2(DBDl)+2Fe3O4+H2O(g)	-3.81	-3.95	-2.64	8.58E+01	1.93
42	TBM	g	Fe_2O_3	c		dibutyl disulfide (DBDg)	g	Fe_3O_4	c	H_2O	g	C4H10S(2M2Pg)+3/2Fe2O3↔1/2C8H18S2(DBDg)+Fe3O4+1/2H2O(g)	5.84	13.80	1.73	5.44E-02	-1.26
43	TBM	g	Fe_2O_3	c		dibutyl disulfide (DBDg)	g	Fe_3O_4	c	H_2O	g	2C4H10S(2M2Pg)+3Fe2O3↔C8H18S2(DBDg)+2Fe3O4+H2O(g)	11.68	27.60	3.45	2.96E-03	-2.53
44	TBM	l	Fe_2O_3	c		dibutyl disulfide (DBDl)	l	Fe_3O_4	c	H_2O	g	2C4H10S(2M2Pl)+3Fe2O3↔C8H18S2(DBDl)+2Fe3O4+H2O(g)	10.98	38.47	-0.49	2.27E+00	0.36
45	TBM	g	FeO(OH)	c		dibutyl disulfide (DBDg)	g	Fe_3O_4	c	H_2O	g	2C4H10S(2M2Pg)+6FeO*OH↔C8H18S2(DBDg)+2Fe3O4+4H2O(g)	51.24	139.05	9.78	6.75E-08	-7.17
46	TBM	g	FeO(OH)	c	H_2(g)	n-butane (Bl)	l	FeS	c	H_2O	g	C4H10S(2M2Pg)+FeO*OH+1.5H2(g)↔C4H10(Bl)+FeS+2H2O(g)	-15.43	17.86	-20.75	1.64E+15	15.21
47	TBM	g				n-butane (NBAg)	g	S_8	g			C4H10S(2M2Pg)↔C4H10(NBAg)+1/8S8(g)	-1.24	6.35	-3.14	1.99E+02	2.30
48	TBM	g				n-butane (Bl)	l	S_8	g			C4H10S(2M2Pg)↔C4H10(Bl)+1/8S8(g)	-6.35	-12.62	-2.59	7.91E+01	1.90
49	TBM	g				n-butane (NBAg)	g	S	c			C4H10S(2M2Pg)↔C4H10(NBAg)+S	-4.27	1.10	-4.59	2.33E+03	3.37
50	TBM	g				n-butane (NBAg)	g	S	g			C4H10S(2M2Pg)↔C4H10(NBAg)+S(g)	69.38	54.75	53.06	1.27E-39	-38.90
51	TBM	l				n-butane (NBAg)	g	S_8	g			C4H10S(2M2Pl)↔C4H10(NBAg)+1/8S8(g)	6.16	27.56	-2.06	3.23E+01	1.51
52	TBM	l				n-butane (Bl)	l	S_8	g			C4H10S(2M2Pl)↔C4H10(Bl)+1/8S8(g)	4.38	35.94	-6.33	1.29E+01	1.11
53	THT	g	Fe	c		isobutene (2MPg)	g	FeS	c			C4H8S(TCPg)+Fe↔C4H8(2MPg)+FeS	-20.31	4.39	-21.61	6.99E+15	15.85
54	THT	g	Fe	c		n-butene (1BTg)	g	FeS	c			C4H8S(TCPg)+Fe↔C4H8(1BTg)+FeS	-16.34	6.70	-18.34	2.76E+13	13.44

R=Reactant; P=Product; Ph=Phase (c=solid, l=liquid, g=gas)
DMS=dimethyl sulfide; EM=ethyl mercaptan; IPM=isopropyl mercaptan; MES=methly ethyl sulfide; NBM=normal butyl mercaptan; TBM=tertiary butyl mercaptan; THT=tertrahydrothiophene

Table 9. Vapor Pressures of Selected Hydrofracturing Chemicals

Compound	T (°C)	T (K)	Vapor Pressure (mm Hg)	Temperature Range (K)	Antoine Equation Parameters*			Reference
					A	B	C	
1-Butanol	20	293	4.5	295.7 - 390.9	4.54607	1351.56	-93.34	http://webbook.nist.gov/cgi/cbook.cgi?ID=C71363&Mask=4#Thermo-Phase
2,2-dibromo-3-nitrilopropionamide (DBNPA)	25	298	2.0E-05					http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_0043/0901b80380043c9e.pdf?filepath=biocides/pdfs/noreg/253-01464.pdf&fromPage=GetDoc
2-Ethylhexanol	20	293	0.08	347.22 - 456.70	4.01389	1325.95	-126.68	http://webbook.nist.gov/cgi/cbook.cgi?ID=C104767&Units=SI&Mask=4#Thermo-Phase
2H-1,3,5-thiadiazine-2-thione, tetrahydro-3,5-dimethyl-	68	341	17.5					https://www2.itap.purdue.edu/msds/docs/12462.pdf
2H-1,3,5-thiadiazine-2-thione, tetrahydro-3,5-dimethyl-	68	341	2.77					http://cameochemicals.noaa.gov/chemical/18086
2-n-Butoxy-1-ethanol	20	293	0.54	365.7 - 443.3	4.25626	1511.41	-88.815	http://webbook.nist.gov/cgi/cbook.cgi?ID=C111762&Units=SI&Mask=4#Thermo-Phase
2-Propyn-1-ol/Propargyl alcohol	20	293	11.6					http://www.chemicalbook.com/CASEN_107-19-7.htm
3(2H)-isothiazolone, 2-methyl-	25	298	<0.1					http://www.chemicalbook.com/ChemicalProductProperty_EN_CB0193926.htm
Acetic acid	20	293	12	290.26 - 391.01	4.68206	1642.54	-39.764	http://webbook.nist.gov/cgi/cbook.cgi?ID=C64197&Mask=4#Thermo-Phase
Acetic acid anhydride	20	293	4	335.99 - 412.57	4.24655	1427.77	-75.113	http://webbook.nist.gov/cgi/cbook.cgi?ID=C108247&Units=SI&Mask=1EFF#Thermo-Phase
Benzene, 1,2,4-trimethyl-	20	293	1.4	357.9 - 443.53	4.16873	1573.27	-64.586	http://webbook.nist.gov/cgi/cbook.cgi?ID=C95636&Mask=4 (7 of 7)
Benzene, 1,2-diethyl-	20	293	0.69	369.88 - 457.64	4.11506	1577.89	-72.596	http://webbook.nist.gov/cgi/cbook.cgi?ID=C135013&Mask=4#Thermo-Phase
Benzene, 1,3,5-trimethyl-	20	293	1.7	354.64 - 438.87	4.19927	1569.62	-63.572	http://webbook.nist.gov/cgi/cbook.cgi?ID=C108678&Mask=4 (1 of 7)
Ethylbenzene	20	293	7.1	329.74 - 410.27	4.07488	1419.32	-60.539	http://webbook.nist.gov/cgi/cbook.cgi?ID=C100414&Mask=4#Thermo-Phase
Ethylene glycol	20	293	0.058					http://www.cheric.org/research/kdb/hcprop/showcoef.php?cmpid=909&prop=PVP
Formaldehyde	20	293	3268	163.76 - 250.86	4.28176	959.43	-29.758	http://webbook.nist.gov/cgi/cbook.cgi?ID=C50000&Mask=4#Thermo-Phase
Glutaral/Glutaraldehyde	25	298	0.58					http://www.lookchem.com/Glutaraldehyde/
Isopropyl alcohol	20	293	31	329.92 - 362.41	4.861	1357.43	-75.814	http://webbook.nist.gov/cgi/cbook.cgi?ID=C67630&Mask=4#Thermo-Phase
Methyl alcohol	20	293	97	288.0 - 356.83	5.20409	1581.34	-33.5	http://webbook.nist.gov/cgi/cbook.cgi?ID=C67561&Mask=4#Thermo-Phase
Monoethanolamine (MEA)	21	294	0.26					http://www.chem-group.com/services/mea-vapor.tpl
Toluene	20	293	22	273.13 - 297.89	4.23679	1426.45	-45.957	http://webbook.nist.gov/cgi/cbook.cgi?ID=C108883&Mask=4 (2 of 10)
Xylene (-p)	20	293	6.6	286.43 - 452.38	4.14553	1474.4	-55.377	http://webbook.nist.gov/cgi/cbook.cgi?ID=C106423&Mask=4#Thermo-Phase

*$\log_{10}(P) = A - (B / (T + C))$ A,B,C = Antoine Equation Parameters P = vapor pressure (bar) T = temperature (K)

Although odor fade is generally recognized in the gas industry and has led to the practice of pickling new (or old) lines, there has been little in the literature in terms of the quantity of odorant or duration that might be required to “quench” the reactivity of pipe or “condition” the line. Table 10 summarizes data from four recent case studies of pre-odorization/ pickling.[21,27,42,45] The results indicate that by using the technique of injection of highly odorized gas, (TBM or TBM/IPM and MES blends), some 0.2 to 0.4 mL/ft^2 of odorant addition was required to achieve full conditioning of 6-inch pipe. Nearly double the odorant addition rate was required when using the continuous liquid addition technique. The odorant addition rate was significantly lower (0.05 mL/ft^2) when using THT, as expected due to its known lower reactivity.

Table 10. Literature Case Studies of Pickling/Conditioning of New Natural Gas Steel Pipe

Reference #[a]	1		2					1				3		4	
Pipe length[b], miles	38.6	10.3	0.19	0.19	0.19	0.19	0.19	4.8	7.1	10.5	4.8	1.1		21.7	27.3
NPS, inches	6	8	2	4	6	8	12	6	6	6	6	12		12	10
Gas flow rate, SCFH	NS	28.3	NS	NS	NS	NS	NS	28.3	28.3	42.5	NS	No flow[i]	6.7[j]	Various	Various
Gas pressure, psig	261	261	NS	NS	NS	NS	NS	102	87	65	87	8	42	435	943
Injection Technique[c]	CL	CL	CL	CL	CL	CL	CL	HG	HG	HG	HG	Liquid Slug	CL	CL	CL
Odorant[d]	TBM/IPM		TBM/MES					TBM/IPM				TBM		THT	
Duration[e], hours	1008	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	504	120	72	48
Odorant Addition[e], mL/ft	1.2	1.5	0.09	0.17	0.26	0.34	0.52	0.61	0.46	0.61	0.61	0.66	2.47	0.17	0.14
Odorant Addition, mL/ft^2	0.79	0.74	0.16	0.16	0.16	0.16	0.16	0.39	0.30	0.39	0.39	0.21	0.79	0.050	0.047
Odorant Level[f], ppmv	NS	NS	NS	NS	NS	NS	NS	41[f]	41[f]	41[f]	41[f]	>15 to 0[g]	2-3 to 0[h]	39[k]	39[k]

NS=Not Specified ft=foot mL=milliliter or 1 cm^3 NPS=Nominal pipe size

ppmv=parts-per-million by volume psig=pounds-per-square inch SCFH=Standard cubic foot per hour

[a] Reference #:

1. Larcher, A. V. and Bromly, J. H., “Rapid Odorant Conditioning of New Natural Gas Lines,” Paper # 934, 9th APCChE Congress, Christchurch, New Zealand, Sept. 29-Oct. 3, 2002.

2. Kopidlansky, R. L., “Odorant Conditioning of New Distribution Systems,” Natural Gas & LP Odorization Case Study & Best Practices Workshop, July 21-22, 2003, Minneapolis, MN, Paper no. Odor-13-5-5, 4pp.

3. Ivanov, I., Strmen, J. and Jones, L., "Pre-Odorization or "Pickling" of New Natural Gas Pipe," Pipeline & Gas Journal, Vol. 236, No. 11, Pages 50-54, November 2009.

4. de Renty, M. et al., "Uncoated Steel Pipes Commissioning: GDF SUEZ Experience with THT," International Gas Union Research Conference, IGRC Paris 2008, Paper 240, 15pp.

[b] Data shown in reference #2 were based on 1000 ft (0.19 miles) of pipe , not on actual total length of pipe pickled.

[c] Injection Technique

CL=Continuous liquid dosing (controlled and continuous flow of liquid odorant)

HG=Injection of "highly odorized gas" employing a by-pass odorizer configured so that the resulting gas entering the section to be conditioned typically contained approximately 10 times the nominal odorant target concentration

[d] Odorant

TBM/IPM=Spotleak 1003 (Atofina (Australia) Pty Ltd.)–80% t-butylmercaptan (TBM)+20% i-propylmercaptan (IPM)

TBM=100% t-butylmercaptan

THT=100% tetrahydrothiophene

[e] To fully condition the pipe

[f] In "highly odorized gas"

[g] Level of >15 ppmv at end of pipe just after flaring over-odorized gas dropped to 0 ppm (by Draeger tube) after 3 weeks.

[h] During continuous controlled odorant injection phase (following initial slugging phase), odorant level at end of pipe dropped from 2-3 ppmv to 0 ppmv after stopping injection over 10-week post-injection monitoring period.

[i] Phase 1 of project

[j] Phase 2 of project

[k] At end of pipe

To obtain specific detailed data from project stakeholders, two survey questionnaires were completed and emailed to selected company technical contacts after an initial phone contact. The first survey form (Table 11) focuses on pipeline odor fade events and the second (Table 12) on pre-conditioning (pickling) and supplemental odorization. Also included with the second survey are three tables in Excel format with additional detailed questions (Table 13 and Table 14) to be filled out.

Five surveys were received from members of the project Steering and Technical Committees. The results are presented in Table 15 through Table 23. It should be noted that any responses that might identify the respondent have been omitted. In general, the odor fade survey results indicated that:

- Most odor fade events were reported to have been prompted by weak sniff test results and most respondents reported performing follow-up quantitative analyses.
- No instances of solvent odors were reported.
- Two odor fade events were reported with plastic (PE) pipe, the others with steel pipe.
- Ambient temperature ranged from 20-90°F
- All events involved a single gas source of natural gas.
- No pipe cleaning was mentioned as having been employed by any of the respondents
- Odorants involved were Spotleak 1009 (IPM:TBM) or 1410 (DMS:TBM) and TBM:THT (50:50); no odorizer operational issues were noted.
- Supplementary odorant injection was employed to increase odorant levels by all but one of the respondents.

One respondent commented that when new pipe is placed in service normal flows and normal odorant dosages are applied, which in their case is four times the legal limit of odorant and is considered "conditioning". It was also mentioned that there are sometimes issues if the new pipe is stagnant for long periods of time.

Another respondent commented that: “…we have locations in our system that had at one time required between 0.5 to 1.0 lb/mmcf to odorize to 1/10th the lower explosive limit (LEL) that now require 2 to 4 lb/mmcf to reach the same odorization level. The gas is all being delivered by other interstate pipelines located here…my guess being that we are now receiving gas from a non-traditional source. The other issue was related to a large landfill coming online; (our odorant) would not odorize the gas stream. The solution to that was to switch to (another odorant), which seems to be odorizing the gas adequately.”

Table 11. Odor Fade Event Survey

ODOR FADE EVENT SURVEY

Prepared by

Gas Technology Institute
Des Plaines, IL 60018

The Gas Technology Institute is currently conducting a study collecting, analyzing, and evaluating data on natural gas and propane odor fade events. Please fill in the information requested below using as many lines to answer each question as needed and a separate form for each event. Also, state if data not available for a particular question.

Description of event and pipeline conditions

1. Event date:
2. Location (city/state):
3. Reported by whom?:
4. Was sniff/olfactory testing performed at the time of the event and what were the results?:
5. Was odorant level determined by quantitative analysis instrumentation, such as titrators, analyzers or chromatographs?
    A. What were measured odorant levels?:
6. Any unusually strong solvent odors?:
7. What was the natural gas composition (major, minor and trace components)?:
8. List of affected system parts:
9. Provide brief chronology of event:
10. Type of customers (residential, commercial, or industrial):
11. Number of customers:
12. Pipeline material(s) (e.g., plastic, steel, internally-coated steel):
13. Pipe in-service age(s) (e.g., recently installed, old, etc.):
14. Pipe storage history and location before installation (e.g., outside for x years):
15. Ambient temperature:
16. Length(s) of pipe involved:
17. Diameter(s) of pipe involved:
18. Normal pipeline pressure(s):
19. Gas flow rate(s) at time of event:
20. Pipeline terrain (e.g., any low points or river crossings?):
21. Single or multiple gas sources (e.g., unconventional gas involved?):
22. Any upstream upsets or significant flow variations noted around time of event?:
23. Normally used odorant composition(s) and concentration/level:

24. Type of nearest odorizer(s):
25. Location/distance of nearest odorizer(s):
26. Was odorizer(s) functioning properly at all times?:
27. How long was pipeline in service with gas flow before event occurred?:
28. Was pipeline pickled/conditioned at installation/commissioning?:
    A. If yes, also fill out GTI pipeline pickling/conditioning survey
29. How was odorant fade event resolved?
    A. Supplementary odorant injection? (If this method was used, also fill out GTI pipeline pickling/conditioning survey)
    B. Gas flow rate or pressure change (specify from-to)?:
    C. Main line odorizer rate increase (specify from-to and duration)?:
    D. Other (please specify details)?:
30. For how long after the event was the odorant level monitored (and method) and are these data available?:

Table 12. Natural Gas Pipeline Pickling/Conditioning Process Survey

NATURAL GAS PIPELINE PRE-ODORIZATION (PICKLING/CONDITIONING) PROCESS SURVEY

Prepared by

Gas Technology Institute
Des Plaines, IL 60018

The Gas Technology Institute is currently conducting a study collecting, analyzing, and evaluating data on natural gas pipeline pickling/conditioning processes in conjunction with a GTI/OTD project relating to odor fade prevention. Please fill in the information requested below using as many lines to answer each question as needed and a separate form for each event. Also, state if data not available for a particular question.

Question 1: How many pipeline pickling/conditioning projects have been conducted by your company within the last ten years on newly installed/commissioned and old pipelines?

Answer 1: New Pipelines: Old Pipelines:

Question 2: How was the type of pickling/conditioning process(es) such as slug dosing, highly odorized gas, etc., generally selected for each project? (e.g., previously used at company, by company engineer, recommended by consultant or odorant supplier, etc.)

Answer 2:

Question 3: How was the amount of odorant initially injected and/or the odorant injection rate(s) used for the pickling/conditioning process(es) generally determined for each project? (e.g., previously used by company, by company engineer, by consultant or odorant supplier, etc.)

Answer 3:

Question 4: Was any pickling/conditioning project prompted by an odor fade situation/event?

Answer 4: (If yes, fill in GTI Odor Fade Event Survey for each project)

Please fill in the Excel tables in the accompanying attached file containing additional questions about the pickling/conditioning project(s) conducted. Priority should be given to those projects with the most quantitative data.

Table 13. Additional Questions for the Pipeline Gas Pipeline Pickling/Conditioning Survey (in Microsoft Excel format), part 1

Project No.	Customer Type & No.		Natural Gas Composition Available		Gas at Beginning of Project		Low Point(s) in the Terrain		Pipe Laid on a River Bed		Hydrostatic Testing Conducted after Project		Water Content, lb/MMCF (after hydrostatic testing)
	Residential=R Commercial=C Industrial=I	No.	Yes	No	Conditions	Water Content, lb/MMCF	Yes	No	Yes	No	Yes	No	

Project No.	Odorization Process Phase (in order of application)							Odorant Type				Odorant Dosage				Natural Gas Flow			
	Static Slug Dosing	Highly Odorized Gas	Continuous Liquid Dosing	Other A (specify)	Other B (specify)	Other C (specify)	Other D (specify)	Phase #				Phase #				Phase #			
								1	2	3	4	1	2	3	4	1	2	3	4

Table 14. Additional Questions for the Pipeline Gas Pipeline Pickling/Conditioning Survey (in Microsoft Excel format), part 2

Project No.	Ambient Temperature				Excess or Over-odorized Gas Flared				Type of Odorization Equipment Used			
	Phase #				Phase #				Phase #			
	1	2	3	4	1 (Y/N)	2 (Y/N)	3 (Y/N)	4 (Y/N)	1	2	3	4

Project No.	Duration				Time Lag between Phases (Y/N)			Total Odorant Injected				Odorant Level at Pipe End			
	Phase #							Phase #				Phase #			
	1	2	3	2	1-2	2-3	3-4	1	2	3	4	1	2	3	4

Table 15. Odor Fade Survey Results (Part 1)

Question	Response		
Event date	2002	2008	2009
Reported by	Technician	Technician	Design Engineer
Was sniff/olfactory testing performed at the time of the event and what were the results?	Yes, multiple reads over 6-8 weeks	Yes, multiple reads over 6-8 weeks	Yes, multiple reads over 1 week
Was odorant level determined by quantitative analysis instrumentation, such as titrators, analyzers or chromatographs?	Yes	Yes	No
What were measured odorant levels?	Not available	Not available	None
Any unusually strong solvent odors?	No	No	No
What was the natural gas composition (major, minor and trace components)?			Unknown
List of affected system parts			
Provide brief chronology of event	1) Highway project to install approximately 7.8 miles of PE pipe (2"-6" pipe size), completed 12/30/2001. 2) Weak "sniff test" reads in February, week of 2/18. 3) Increased injection rates, week of 2/18. 4) Installed temporary odorizer, week of 2/25. 5). Monitored odor levels, leak calls 2/15-4/1. 6) Deactivate temporary odorizer 4/1.	1) Weak "sniff test" reads on 6/27. 2) Install temporary odorizer 7/3. 3) Monitor odor levels, leak calls 6/27-7/21. 4) Deactivate temporary odorizer 7/21.	1) Highway project to install approx 3 miles of PE pipe (6" pipe size), completed 7/30/2009. 2) Set up temporary odorizer at purge location. 3) Odorizer operates in time mode. 3) Purge new main with nitrogen, followed by natural gas. 4) Set odorizer to operate at 10 second interval. 5) Monitor odor levels (sniff tests), leak calls. 6) Deactivate temporary odorizer 7/30/2009.
Type of customers (residential, commercial, or industrial)	Residential, commercial	Residential, commercial	Residential
Number of customers	Approximately 5000	Approximately 5000	Approximately 1500
Pipeline material(s) (e.g., plastic, steel, internally-coated steel)	New PE	Plastic, steel	New PE
Pipe in-service age(s) (e.g., recently installed, old, etc.)	Recently installed	Various	Recently installed
Pipe storage history and location	Unknown	None	Delivered from supplier to site
Was pipe supplier changed?	Unknown	No	No
Ambient temperature	20-40°F	70-80°F	70-80°F
Length(s) of pipe involved	7.8 miles	Several miles	3 miles
Diameter(s) of pipe involved	2"-6"	Various, 2"-8"	6"
Normal pipeline pressure(s)	Low to 60 psig	60 psig	40 psig
Gas flow rate(s) at time of event	Unknown	Unknown	Unknown
Pipeline terrain (e.g., any low points or river crossings?)	River crossing	Various	Cross-country
Single or multiple gas sources (e.g., unconventional gas involved?)	Single	Single	Single
Any upstream upsets or significant flow variations noted around time of event?	None	None	None
Was recent cleaning (pigging or scraping) performed and, if so, what cleaning liquids were used?	None	None	Pigging with foam pig, no liquids used
Normally used odorant composition(s) and concentration/level:	Spotleak 1009, 0.5 lb/mmcfh	Spotleak 1009, 0.5 lb/mmcfh	Spotleak 1009, 0.5 lb/mmcfh
Type of nearest odorizer(s)	Peerless	YZ Systems	YZ Systems
Location/distance of nearest odorizer(s)	10-15 miles	20-22 miles	5 miles
Was odorizer(s) functioning properly at all times?	Yes	Yes	Yes
How long was pipeline in service with gas flow before event occurred?	2-4 weeks		New
Was pipeline pickled/conditioned at installation/commissioning?	No	Unknown	Yes
How was odorant fade event resolved?			
Supplementary odorant injection?	Yes	Yes	Yes
Gas flow rate or pressure change?	No	No	No
Main line odorizer rate increase?	Yes, 2/18-4/1	No	No
Other?			
For how long after the event was the odorant level monitored (and method) and are these data	Increased survey points for next 3 months, continuous for normal survey points	Increased survey points for next 3 months, continuous for normal survey points	Continuous for normal survey points

*Blank indicates no response

Table 16. Odor Fade Survey Results (Part 2)

Question	Response		
Event date	Oct 2008-ongoing	March 2008-ongoing	N/A
Reported by	Customer Service	Customer Service	Employee
Was sniff/olfactory testing performed at the time of the event and what were the results?	Absent or weak odor	Weak odor	Yes
Was odorant level determined by quantitative analysis instrumentation, such as titrators, analyzers or chromatographs?	Yes		No
What were measured odorant levels?	0.03 ppm	0.4 ppm of THT	N/A
Any unusually strong solvent odors?	No	No	No
What was the natural gas composition (major, minor and trace components)?	Methane, ethane, propane, butane, N2, C6+, O2, CO2	Methane, ethane, propane, butane, N2, C6+, O2, CO2	Unknown
List of affected system parts	Whole houseline	Whole houseline	Entire line
Provide brief chronology of event	Event reported on Oct 2008	Event reported on March 2008	
Type of customers (residential, commercial, or industrial)	Residential	Commercial	Residential
Number of customers	Multiple (apartment building)	1	5
Pipeline material(s) (e.g., plastic, steel, internally-coated steel)	Carbon steel	Carbon steel	Steel
Pipe in-service age(s) (e.g., recently installed, old, etc.)	Recently installed	Old – from mid 80s	Recently installed
Pipe storage history and location	Unknown	Installed in ground with gas at 45 psig (STAGNANT–DEAD END)	
Was pipe supplier changed?	Pipe supplier was chosen by the customer-contracted plumber	Unknown	No
Ambient temperature	65°F	65°F	
Length(s) of pipe involved	~650 ft	1350 ft	20 km
Diameter(s) of pipe involved	2", ¾", ½"	10"	NPS 6 (10 km), NPS 4 (10 km)
Normal pipeline pressure(s)	5 psig	45 psig	150 psi
Gas flow rate(s) at time of event	5 SCFH	20 SCFH	Negligible
Pipeline terrain (e.g., any low points or river crossings?)	10-story building	Flat	Standard terrain—no low points, no river crossings
Single or multiple gas sources (e.g., unconventional gas involved?)	Single	Single	Single
Any upstream upsets or significant flow variations noted around time of event?	No	No	No; newly installed line; low flow
Was recent cleaning (pigging or scraping) performed and, if so, what cleaning liquids were used?	No	No	N/A
Normally used odorant composition(s) and concentration/level:	50:50 TBM:THT (some supplies come pre-odorized with IPM/TBM)	TBM/THT 50:50, 1.5 ppm	Spotleak 1410
Type of nearest odorizer(s)	YZ	YZ	Dosador
Location/distance of nearest odorizer(s)	30 miles	250 miles	At gate station
Was odorizer(s) functioning properly at all times?	Yes	Yes	Yes
How long was pipeline in service with gas flow before event occurred?	Event occurred at customer turn on	Event occurred at customer turn on	
Was pipeline pickled/conditioned at installation/commissioning?	Yes	Yes	No
How was odorant fade event resolved?			
Supplementary odorant injection?	Yes	Yes	
Gas flow rate or pressure change (specify from from-to)?	No	No	
Main line odorizer rate increase (specify from-to and duration)?	No	No	
Other (please specify details)?	NA	NA	Operating at 350 psi, load the line up at 350 psi and let it drop down to 150 psi then turn the top run back on, simulated flow
For how long after the event was the odorant level monitored (and method) and are these data available?	On going, 2+ yrs	On going, 2+ yrs	

*Blank indicates no response

Table 17. Odor Fade Survey Results (Part 3)

Question	Response	
Event date	May 2010	1993
Reported by	Employee	Employees
Was sniff/olfactory testing performed at the time of the event and what were the results?	Yes; barely detectable. However, after injecting odorant and purging the results were detectable and strong in some areas.	Exact numbers from sniff test are no longer available, but odor was described as very weak or even non-existent.
Was odorant level determined by quantitative analysis instrumentation, such as titrators, analyzers or chromatographs?	Yes; SRI 8610C gas chromatograph	Titrators were used, but resulting data has been lost.
What were measured odorant levels?	They vary (please see attached case study)	N/A
Any unusually strong solvent odors?	No	No
What was the natural gas composition (major, minor and trace components)?	DMS:TBM 25:75.	Nothing unusual. Gas BTU is typically around 1040-1060.
List of affected system parts		All distribution piping
Provide brief chronology of event	Several attempts were made to accelerate the odorant conditioning of this pipeline including injecting 5 L of raw odorant by methods of dripping and slugging, closing valves at appropriate stations to increase the flow rate and push the odorized gas through the line. Although the above procedures slightly improved the odor levels, many were temporary and concentrations were still low. The following procedure was then used to improve the the pipeline odorization. Three injection points were fabricated to pickle the steel pipeline. The flow of the odorant was to be dictated by the purging apparatus downstream. The purging would be done at the end of the XHP (extra high pressure) steel main. A temporary station was installed to lower the pressure from 400 psi line to 80 psi. A purging assembly was fabricated. Once the purging had begun, a 4-L portable injector was used to add odorant to the natural gas by injecting it into the second injection point. Injection points one and three were not used in this procedure. The total purge time was 2 hours and 5 minutes. The total odorant injection time (using all 4 L of odorant) was 1 hour and 44 minutes. The odorant levels were left at high concentrations after the purging and injection procedure. In order to ensure the levels remained detectable they were monitored weekly. After two weeks the levels dropped back down to barely detectable and a meeting was held to determine the next steps. It was decided that the purging and odorant injection procedure needed to be repeated in order to fully condition the line. The second procedure was done three weeks after the first on March 31, 2010. It was decided that two purging assemblies would be fabricated to ensure the odorized natural gas would travel to the polyethylene mains (which are attached to the steel NPS 6 main). A 1-L portable injector was used to add odorant to the natural gas by again injecting it into the second injection point. After monitoring the odorant levels since the second purge, results showed that the pipelines remained relatively stable and continued to be classified as "detectable" at 1.0 % gas-in-air at each location. The temporary station was recently decommissioned and the pressure was retuned to normal operating conditions of approximately 400 psi. Odorant levels are continuing to be monitored.	A new 10" and 8" pipeline approximately 209 miles long was constructed in 1987-1988. Although the line was initially slugged with odorant, the smell faded after a few months. Several times over a five year period, additional odorant was added (slugged) approximately 20 miles from the end of the line where the fading was occurring.
Type of customers (residential, commercial, or industrial)	Residential	Combination of all, but primarily residential
Number of customers	Approximately 240	This was a new area – one that did not have gas prior to this so it started out with very few customers and gradually grew.
Pipeline material(s) (e.g., plastic, steel, internally-coated steel)	Steel	Steel (no internal coating) high pressure line with plastic distribution system.
Pipe in-service age(s) (e.g., recently installed, old, etc.)	Recently installed	All pipe was new
Pipe storage history and location		Unknown
Was pipe supplier changed?	No	No
Ambient temperature	Not measured	Typically 40's in winter, 90's in summer
Length(s) of pipe involved	7.5 miles of NPS 6 steel pipe	209 miles for entire steel line, but only last 20 miles had odor fading
Diameter(s) of pipe involved	NPS 6 steel	8" steel, 2-6" plastic
Normal pipeline pressure(s)	XHP approximately 400 psi	500 psi on steel, 45 psi on plastic
Gas flow rate(s) at time of event		Unknown, but varied. Flow rates were relatively low as it started out with no customers.
Pipeline terrain (e.g., any low points or river crossings?)	No	Mountainous area – three river crossings in fade area.
Single or multiple gas sources (e.g., unconventional gas involved?)		Single source, conventional gas
Any upstream upsets or significant flow variations noted around time of event?	No	None
Was recent cleaning (pigging or scraping) performed and, if so, what cleaning liquids were used?	No	Line had recently been tested with water. Line was dried using foam pigs.
Normally used odorant composition(s) and concentration/level:	TBM:DMS – 75%:25%	50/50 THT/TBM odorized at 0.75 lb/MMCF at the beginning of the line.
Type of nearest odorizer(s)		Injection pump
Location/distance of nearest odorizer(s)		Odorizer was approximately 190 miles from odor fade area.
Was odorizer(s) functioning properly at all times?		Yes
How long was pipeline in service with gas flow before event occurred?	The pipeline was installed in Sept. 2006	Fading started soon after line was put in service
Was pipeline pickled/conditioned at installation/commissioning?	Yes	Yes
How was odorant fade event resolved?		
Supplementary odorant injection?	Yes; odorant was injected and the line was purged.	Supplemental odorizer installed at block valve assembly and gas was odorized at .5 lbs/MMCF
Gas flow rate or pressure change?	Yes; pressure change from approximately 400 psi to 80 psi for 12 months. Then the pressure was brought back up to 400 psi after 1 year. If odorant begins to fade again pressure will be brought down again.	Additional regulation dropped pressure to 200 psi.
Main line odorizer rate increase?	No	Left primary odorizer at start of line at 0.75 lbs/MMCF
Other?	No	
For how long after the event was the odorant level monitored (and method) and are these data available?	The levels were monitored bi-weekly after first and second odorant injection and purging procedure. Once odorant levels were detectable they were monitored monthly. Since the pressure recently returned to normal operating conditions the odorant levels are continuing to be monitored monthly.	Odor levels rose to normal levels within about a week of cutting pressure and installing supplemental odorization. These measures were kept in place for about a year and then removed. Odor levels have remained normal since then.

*Blank indicates no response

Table 18. Pipeline Pickling/Conditioning Survey Results

Question	Response			
How many pipeline pickling/conditioning projects have been conducted by your company within the last ten years?	New Pipelines: 2; Old pipelines: 1	New Pipelines: 120+; Old pipelines: 2	All newly installed steel pipe has been conditioned (10-20 projects per year or ~120 projects)	New Pipelines: 50; Old pipelines: 5
How was the type of pickling/conditioning process(es) such as slug dosing, highly odorized gas, etc., generally selected for each project? (e.g., previously used at company, by company engineer, recommended by consultant or odorant supplier, etc.)	Company Engineer	Slugs for short lines mainly distribution lines. Continuous method used mainly for transmission where lines are miles long or critical where they need to go inservice right away.	For gate stations, the odorant rate is set at 8 mg/1000m^3 and monitored periodically for 3 to 6 months to ensure that there are detectable readings at the end of the line.	For new pipe segments we have always pickled the line by slug dosing as specified by the company measurement engineer. In all but two cases, old pipelines (pipelines that had been in service more than a few months) that required additional odorant were also slug dosed. Twice we installed supplemental odorizers to give us a boost.
How was the amount of odorant initially injected and/or the odorant injection rate(s) used for the pickling/conditioning process(es) generally determined for each project? (e.g., previously used by company, by company engineer, by consultant or odorant supplier, etc.)	For new pipelines approximately 0.5 lb/mmcfh and for old pipelines adjusted rate based on "sniff test"	Odorant injected using YZ odorizers. Odorant injection rates on slug methods are based on the internal surface are of the pipe @ 0.025 cm^3/ft^2.	The line is energized and purged. A slug of odorant is then put into the line (usually no more than 1 liter) and then odorant is dripped in at a rate of 8 mg/1000 m^3 thereafter.	There are two methods that we have historically used to calculate the volume of odorant needed to pickle. One method is based on the surface area of the pipe to estimate the volume while the other method calculates the volume of gas in the line and then doubles the normal odorant rate for that gas volume. The surface area method always give much higher odorant volumes than the gas volume method so for the first try at pickling we usually use a quatity of odorant between the two calculated values, but closer to the gas volume method (under the theory that it's easier to add additional odorant than remove it.
Was any pickling/conditioning project prompted by an odor fade situation/event?	Yes, 2 projects	Yes, two of them on reported on exisiting company lines, about 16 events reported on new customer hoselines downstream of the meter.	One project	Yes

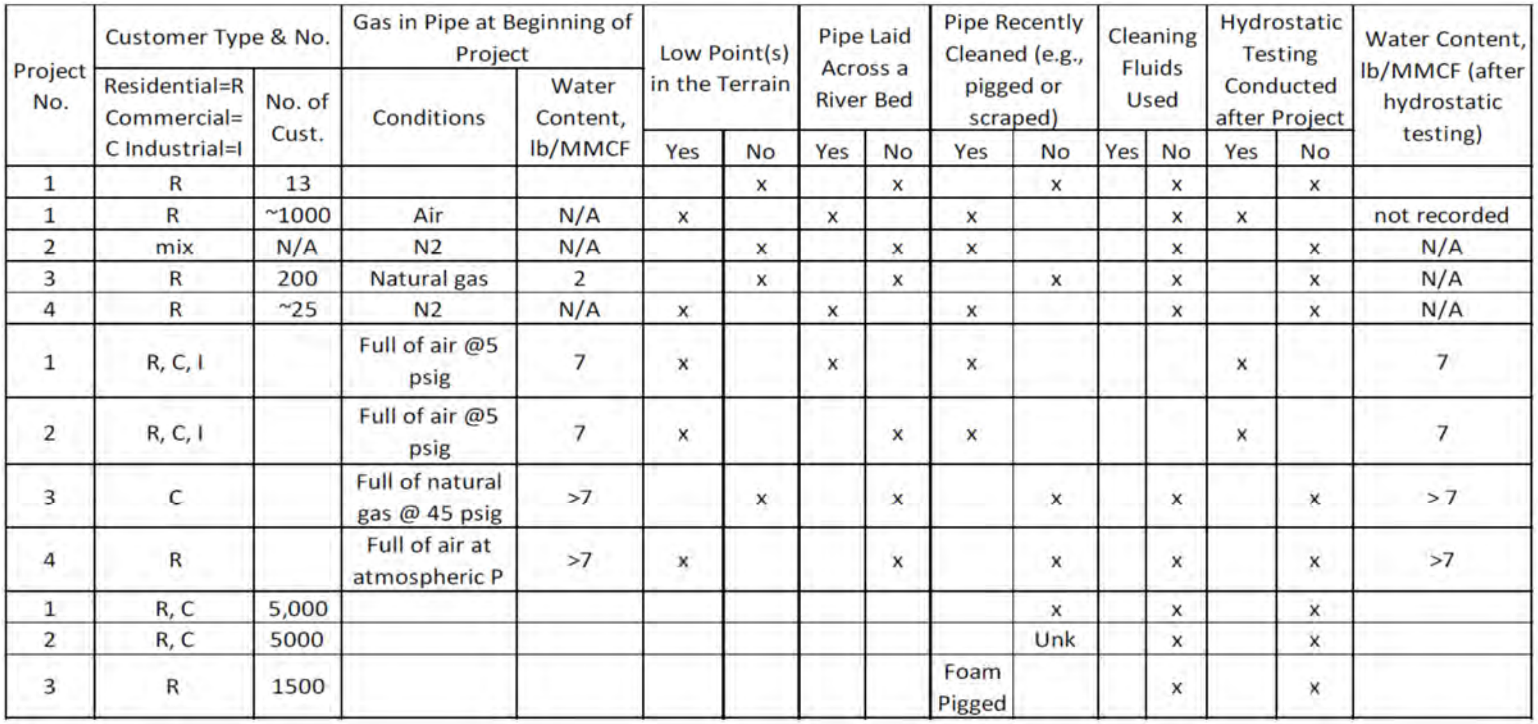
*Blank indicates no response

Table 19. Additional Results for the Pipeline Pickling/Conditioning Survey (Part 1)

Project No.	Pipe Condition (specify)	Pickling/Conditioning Project Dates		Pipe Material		Pipe Length		Pipe Diameter (NPS)		Normal Operating Pressure		Normal Operating Flow		Ambient Temperature		Natural Gas Supply		Natural Gas Composition Available	
		Begin	End	Steel	Plastic											Single	Multiple	Yes	No
1	New Installation (Sept 2006)	2/1/10	3/31/10	x		7.5	mi	6	inch	400	psig			49	F			x	
1	New steel pipe	11/1/88	6/1/94	x		209	mi	8	in	500	psig	unk		30-110	F	x		x	
2	New steel pipe	11/1/10	11/2/10	x		9	mi	20	in	350	psig	unk		35	F	x		x	
3	Old - in service for about 6 years	1/25/11	2/15/11	x		9	mi	6	in	325	psig	160	MCF/D	25	F	x		x	
4	New steel pipe	10/1/09	11/1/09	x		4.5	mi	8	in	340	psig	unk		30	F	x		x	
1	New installation (outside storage ~1 yr)	4/12/09	12/30/09	x		22	mile	24	inch	600	psig	1.5	MMSCFH	70-110	F	x		x	
2	Transition from Oil Line to Gas Line (40s pipe)	5/2/10	Ongoing	x		9	mile	16	inch	450	psig	0.2	MMSCFH	30-80	F	x		x	
3	Old (no flow 20 yrs)	3/2/09	Ongoing	x		1350	ft	10	inch	45	psig	10	SCFH	50-90	F	x		x	
4	New installation (unknown storage)	11/15/08	Ongoing	x		~500	ft	2	inch	5	psig		SCFH	50-80	F	x		x	
1	New installation (prior outside storage unknown)	2/18/02	4/1/02		x	7.8	mile	V	inch	V				30	F	x			x
2	Old	6/27/08	7/21/08	x	x			V	inch	60	psig			75	F	x			x
3	New installation (prior outside storage unknown)	7/27/09	7/30/09		x	3	mile	6	inch	40	psig			75	F	x			x

V=various
Unk=unknown

Table 20. Additional Results for the Pipeline Pickling/Conditioning Survey (Part 2)



Project No.	Customer Type & No.		Gas in Pipe at Beginning of Project		Low Point(s) in the Terrain		Pipe Laid Across a River Bed		Pipe Recently Cleaned (e.g., pigged or scraped)		Cleaning Fluids Used		Hydrostatic Testing Conducted after Project		Water Content, lb/MMCF (after hydrostatic testing)
	Residential=R Commercial=C Industrial=I	No. of Cust.	Conditions	Water Content, lb/MMCF	Yes	No	Yes	No	Yes	No	Yes	No	Yes	No	
1	R	13				x		x		x		x		x	
1	R	~1000	Air	N/A	x		x		x			x	x		not recorded
2	mix	N/A	N2	N/A		x		x	x			x		x	N/A
3	R	200	Natural gas	2		x		x		x		x		x	N/A
4	R	~25	N2	N/A	x		x		x			x		x	N/A
1	R, C, I		Full of air @5 psig	7	x		x		x				x		7
2	R, C, I		Full of air @5 psig	7	x			x	x				x		7
3	C		Full of natural gas @ 45 psig	>7		x		x		x		x		x	> 7
4	R		Full of air at atmospheric P	>7	x			x		x		x		x	>7
1	R, C	5,000								x		x		x	
2	R, C	5000								Unk		x		x	
3	R	1500							Foam Pigged			x		x	

Unk=unknown

Table 21. Additional Results for the Pipeline Pickling/Conditioning Survey (Part 3)

Project No.	Odorization Process Phase (in order of application)							Duration								Time Lag between Phases		
	Static Slug Dosing	Highly Odorized Gas	Continuous Liquid Dosing	Other A (specify)	Other B (specify)	Other C (specify)	Other D (specify)	Phase #								(Yes/No)		
								1		2		3		2		1-2	2-3	3-4
1	1-Initial Slug			2-Lowering the Pressure in the line (No odorant added)	3-odorant Injection & purging at the end of the steel pipeline	4-second odorant Injection & purging at the end of each plastic line	5-Returned Pressure to normal operating conditions (No odorant added)	Not sure		1	wk	3	wk	To present		Y	Y	Y
2	1		2					5	yr	1	yr					N		
3	1							1	d									
4	1-3	5						2	wk	ongoing						N		
5	1-3							3	d									
6	1		1					43								N	N	N
7	1		1					2	d	25	d	9	mo			N	N	N
8	5															Y	Y	Y
9	8															Y	Y	Y
10	N	Y	N					8	wk									
11	N	Y	N					8	wk									
12	N	Y	N					1	wk									

mo=months
wk=weeks
d=days
yr=years

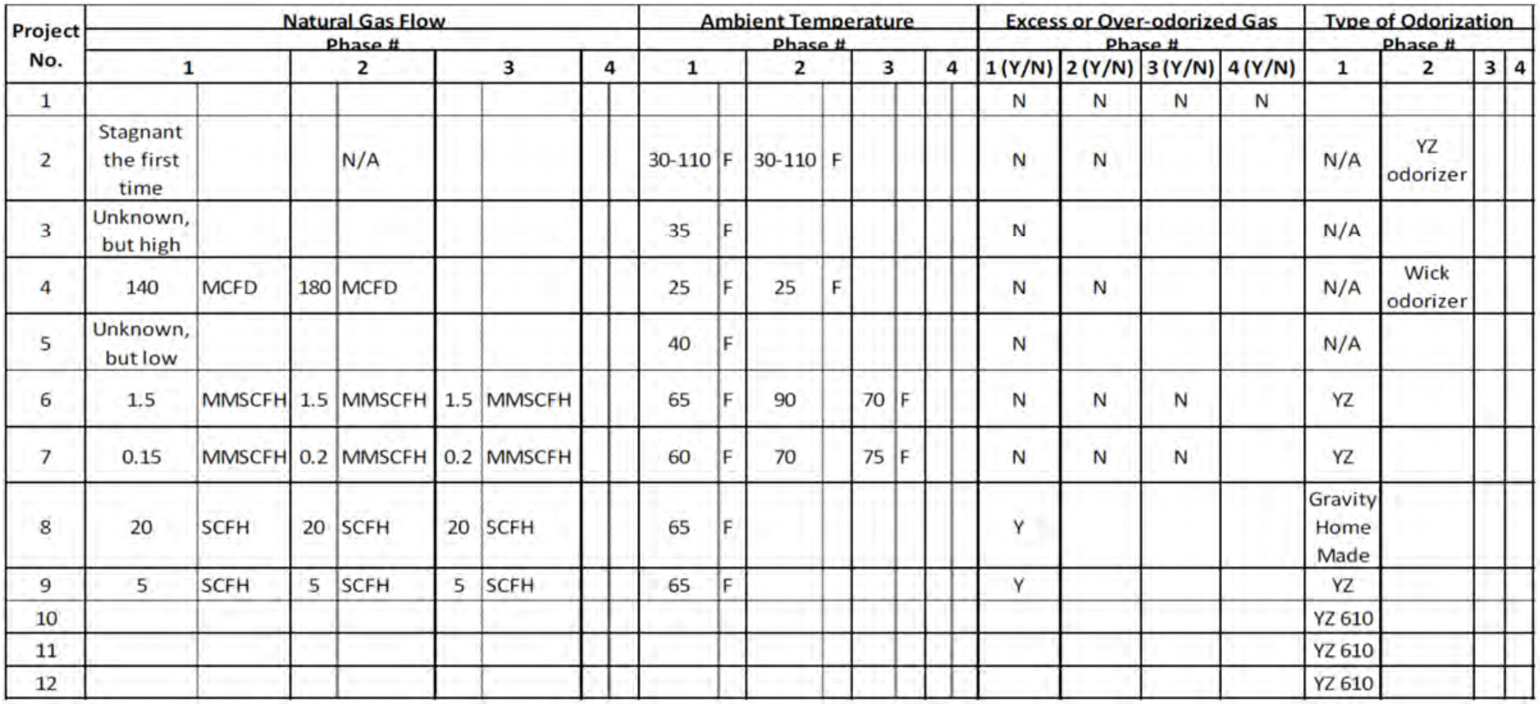
Table 22. Additional Results for the Pipeline Pickling/Conditioning Survey (Part 4)

Project No.	Odorant Type				Odorant Dosage								Measured Odorant Level at Pipe End								Total Odorant Injected							
	Phase #				Phase #								Phase #								Phase #							
	1	2	3	4	1		2		3		4		1		2		3		4		1		2		3		4	
1	TBM & DMS	No odorant was injected in this phase	TBM & DMS	TBM & DMS	Initial slug (not sure)			No odorant was injected in this pahse	4	L	1	L									inital slug (not sure)				4	L	1	L
2	TBM/THT	TBM/THT			Several slugs over the years		0.5	lbs/mmccf					Varied	%gas in air	0.5	%gas in air					N/A		N/A					
3	TBM/THT				20	oz							Not tested								20	oz						
4	TBM/THT	TBM/MES			84	oz	N/A						Varied	%gas in air	0.3	%gas in air					84	oz	N/A					
5	TBM/THT				6, 6, 16	oz							Not tested								28	oz						
6	TBM/THT 50:50	iPr/TBM	TBM/THT 50:50		43	gal	0.2	gal slugs	0.4	lb/MMSCF			43	ppm	30	ppm	1.2	ppm			43	gal	30	gal	203	gal		
7	TBM/THT 50:50	iPr/TBM	TBM/THT 50:50		0.4	lb/MMSCF	0.25	lb/MMSCF	0.4	lb/MMSCF			5	ppm	32	ppm	2.5	ppm			5	gal	32	gal	64	gal		
8	TBM/THT 50:50				3 to 7 cc each time	cc							2-30	ppm							25-50	cc						
9	TBM/THT 50:50				0.1 - 0.5 gal each time	gal							5-450	ppm							0.5-2.5	gal						
10	TBM				0.5	lb/MMSCF																						
11	TBM				0.5	lb/MMSCF																						
12	TBM				0.5	lb/MMSCF																						

L=liter

N/A=not available

Table 23. Additional Results for the Pipeline Pickling/Conditioning Survey (Part 5)



Project No.	Natural Gas Flow							Ambient Temperature							Excess or Over-odorized Gas				Type of Odorization			
	Phase #							Phase #							Phase #				Phase #			
	1		2		3		4	1		2		3		4	1 (Y/N)	2 (Y/N)	3 (Y/N)	4 (Y/N)	1	2	3	4
1															N	N	N	N				
2	Stagnant the first time			N/A				30-110	F	30-110	F				N	N			N/A	YZ odorizer		
3	Unknown, but high							35	F						N				N/A			
4	140	MCFD	180	MCFD				25	F	25	F				N	N			N/A	Wick odorizer		
5	Unknown, but low							40	F						N				N/A			
6	1.5	MMSCFH	1.5	MMSCFH	1.5	MMSCFH		65	F	90		70	F		N	N	N		YZ			
7	0.15	MMSCFH	0.2	MMSCFH	0.2	MMSCFH		60	F	70		75	F		N	N	N		YZ			
8	20	SCFH	20	SCFH	20	SCFH		65	F						Y				Gravity Home Made			
9	5	SCFH	5	SCFH	5	SCFH		65	F						Y				YZ			
10																			YZ 610			
11																			YZ 610			
12																			YZ 610			

Developing a Simplified Odor Fade Model – Laboratory Testing

Prior to the limited field validation testing of the model in Task 5, laboratory batch or “static” testing was needed, and was conducted in this task. The objective was to obtain data regarding the rates of odorant loss under various selected conditions of gas composition, pipe system material and operating system variables, as shown in Table 24 below. The conditions chosen to be tested were limited to those expected to have the greatest effect on odor fade based on past gas quality information[100,101,102,103,104] presented in Table 25 through Table 30.

Table 24. Conditions for Static Testing

Parameter/Variable	Value or Range
Test Duration	Up to 168 hr
Pipe Material	Steel, Plastic
Pipe Length	1.0 ft
Pipe Diameter	2-inch NPS Schedule 40
Pipe Corrosion Level	Control (i.e., passivated) As received Aged
Gas Pressure	60 psig
Temperature	70°F and 34°F
TBM	0-2 ppmv
Water	0-150 lb/MMSCF
Oxygen	0-300 ppmv
Hexanes	0-0.1 mole%
Methanol	0-100 ppmv
Amine (MEA)	50-60 ppmv
Low molecular weight mercaptan	2 ppmv
CH_4	Balance

As TBM is the organosulfur compound most commonly used in natural gas odorants it was selected for initial testing. THT, also widely used, was tested to a lesser extent. Initial tests were conducted using only a nominal 2 ppmv TBM plus pure methane gas mixture without added trace gases present. The TBM loss rate obtained under this condition was compared to that obtained with the added trace components. THT testing used a nominal 4 ppmv THT test gas that consisted of the odorant compound in a synthetic natural gas blend. This mixture was used because it was freshly prepared and available from another project.

The trace constituents water, oxygen, methanol, monoethanolamine (MEA), and hexanes were added to the test pipe at concentrations up to the maximum values shown in Table 24 and could be considered as “worst case normal” conditions in a natural gas pipe system. MEA was selected as a surrogate amine compound representing volatile amine compounds used for natural gas treatment and as a constituent in hydrofracturing fluids. With respect to the oxygen level selected, although significantly higher levels of oxygen in the range of 1-5% have been previously documented in natural gas with propane/air peak shaving and currently in some areas of the US, those high levels could possibly represent worst case conditions.

Table 25. Gas Quality Specifications from Various Gas Transmission Pipeline Companies

	Individual Company						
Item Specified	Southwest US[a]	Southwest US[a]	Midwest US[a]	Southeast US[a]	Midwest US[a]	Western US[h]	Canada[q]
Water, lb/MMCF (max.)	7	7	7	7	7	7[d]	4 [i]
H_2S, grain/100 SCF (max.)	0.5	1.0	0.25	1	0.25	0.25	1 [j]
Mercaptan, grain/100 SCF (max.)	NS [c]	NS	NS	NS	NS	0.3	NS
Total Sulfur, grain/100 SCF (max.)	12	20	20	20	10-20	0.75[e]	5 [k]
CO_2, volume% (max.)	3	3[b]	2	2	3	3	2
O_2, volume% (max.)	1	NS	1	0.5	NS	0.2	0.4
N_2, volume% (max.)	3	3[b]	NS	NS	4[b]	NS	NS
Non-Hydrocarbons, volume % (max.)	4.5	NS	NS	NS	NS	4	NS
Hydrocarbons	NS	NS	NS	NS	NS	45°F[f]	14°F[l]
Temperature, °F	40-120	NS	NS	40-120	40-120	50-105	NS
Heating Value, Btu/SCF	950-1,000	NS	NS	1000 [p]	950-1,100	970 [o]	967 [m]
Hazardous Substances	NS	NS	NS	NS	NS	[g]	NS
Objectionable Materials	NS	NS	NS	NS	NS	NS	[n]

[a] Lyle, Jr., F. F., Burghard, Jr., H. C., and George, E. P., "Effect of Natural Gas Quality on Corrosion in CNG Storage Cylinders-Phase I," New York Gas Group, New York, N.Y., the New York State Energy Research and Development Authority, Albany, N.Y., 1989.

[b] CO_2+N_2

[c] NS=Not Specified

[d] For delivery pressure ≤1,000 psig; 32°F dew point for delivery pressure≥1,000 psig

[e] Includes H_2S, COS, CS_2, mercaptans, and mono- and di- and polysulfides.

[f] Dew point at delivery pressure

[g]Concentrations must not be harful to health, injurious to pipeline or be a limit to marketability (includes carcinogenic and toxic and any substances injurious to pipeline facilities).

[h]Sostek, T., and Vogel, R., "Trace Contaminants in Natural Gas," Institute of Gas Technology, Chicago, Illinois, July 1990.

[i] 65 mg/m^3

[j] 23 mg/m^3

[k] 115 mg/m^3

[l] Dew point at operating pressure

[m] 36 MJ/m^3

[n] "Must not be harmful to health, cause damage to pipeline or make gas unmarketable".

[o] Minimum, dry basis

[p] Minimum

[q] Tiemstra, E., Eng, P., and Cirka, G. E., "Trace Constituents: Experience of NOVA Corporation of Alberta," Institute of Gas Technology, Chicago, Illinois, July 1990.

Table 26. Transmission Pipeline Company Gas Analyses

	Max. Water, lb/MMCF	Max. H_2S, grain/100 SCF	Max. Total Sulfur, grain/100 SCF	Max. CO_2, volume%	Max. O_2, volume% (ppmv)	Max. N_2, volume%	Other Soluble Sulfides, grain/100 SCF
Company A (S&SW US) [b,c]							
High	--[d]	--	--	4.03	--	3.78	--
Low	--	--	--	0.34	--	0.069	--
Average	--	--	--	1.55	--	0.75	--
Company B [b]							
SE US	4	0.020	--	0.99	0	0.32	--
SW US	--	0	--	1.17	0	0.41	--
SE US	--	0	--	0.90	0	0.29	--
NW US	--	0	--	0.91	0	0.29	--
Company C (MW US) [b]							
1	--	--	--	0.41	0.009 (90)	5.91	--
2	--	--	--	0.62	0.009 (90)	3.63	--
3	--	--	--	0.61	0.02 (200)	3.75	--
Company D (SE US) [b]	--	0.056	0.071	1.08	0	0.47	--
Company E (MW US) [b]	--	0.004	0.055	0.49	0.014 (140)	1.05	--
Company F (NE US) [f]							
High	280	0.07	--	0.76	0	2.66	0.57
Low	6	0.01	--	0.39	0	0.36	0.36
Average	52	0.03	--	0.63	0	1.20	0.44
Company G (MW US) [e]	--	--	--	0.43-1.11	--	0.02-0.56	--
Company H (W US) [e]							
High	9.2	0.053	0.24	0.92	--	--	--
Low	1.7	0.001	0.079	0.15	--	--	--
Average	4.7	0.026	0.147	0.538	--	--	--
Company I (NE US) [e]	17	0.6	--	0.01	0.01 (100)	2.9	0.061
Company J (SE US) [e]	--	0.006	0.033	0.59	0.031 (310)	0.41	0.002

[a] Lyle, Jr., F. F., Burghard, Jr., H. C., and George, E. P., "Effect of Natural Gas Quality on Corrosion in CNG Storage Cylinders-Phase I," New York Gas Group, New York, N.Y., the New York State Energy Research and Development Authority, Albany, N.Y., 1989.

[b] Analyses supplied by five interstate gas transmission pipeline companies

[c] 22 samples

[d] Not determined

[e] Analyses supplied by five different distribution companies

[f] Number of samples not reported. Water analyses based on 79 separate dew point determinations at various locations

Table 27. H2S and Water in Natural Gases of 30 Distribution Companies

Company	H_2S		Water, lb/MMCF
	grain/100 SCF	ppmv	
1[b]	1.98[c]	29.8[c]	2-4
2	0.035	0.53	7
3	0.1	1.51	4-7
4	0.05	0.75	3.9-4.0
5	0	0	3
6	0.42	6.32	--
7	0.016	0.24	256
8	0.1	1.51	7
9	0.2	3.01	7
10	0	0	3-4
11	0-1[d]	0-15.1[d]	7-100
12	Nil	Nil	4
13	1[d]	15.1	1
14	0.1	1.51	7
15	0.025	0.38	7
16	0.25	3.76	5-7
17	0.02	0.30	7
18	Nil	Nil	7
19	0	0	--
20	0	0	0
21[b]	0.01	0.15	3-7
22	0.15	2.26	6
23	Clear	Clear	--
24	0.008	0.12	2-3
25	0.011[c]	0.17[c]	2.5
26	0	0	3.4
27	0.022	0.33	7
28	0.3	4.52	7
29	0.03	0.45	6.45
30	Nil	Nil	3.20

[a] Alternative House Piping for Reduced Installation Costs, Engineering Technical Note CSU-86-1-1, American Gas Association, March 1986.

[b] Canadian company

[c] Total sulfur level

[d] Contract level-actual value not reported

Table 28. Test Results of Trace Natural Gas Constituents Sampling and Analysis (Major and Minor Components and C6 Plus Hydrocarbons)

	Median Value	Minimum Value	Maximum Value	Number of Values
Major and Minor Components:				
Moisture, ppmv (lb/MMCF)	120 (6.0)	<10 (<0.50)	2900 (146)	19
Oxygen, ppmv	6.7	2.9	42	19
Helium, mole %	0.024	0.002	0.08	19
Hydrogen, mole %	0.003	<0.001	0.12	19
Nitrogen, mole %	1.15	0.22	2.96	19
Carbon Dioxide, mole %	0.58	0.07	2.62	19
Methane, mole %	95.4	81.1	98.5	19
Ethane, mole %	2.12	0.09	11.8	19
Propane, mole %	0.413	0.005	3.95	19
Isobutane, mole %	0.063	<0.003	0.369	19
n-Butane, mole %	0.055	<0.003	0.82	19
Neopentane, mole %	<0.001	0.0001	0.004	19
Isopentane, mole %	0.019	0.0009	0.18	19
n-Pentane, mole %	0.019	0.0005	0.157	19
C6 & Heavier, mole %	0.042	<0.002	0.226	19
C6 Plus Hydrocarbons, ppmv:				
Aliphatics:				
Cyclopentane	9	<1	50	17
Hexanes	170	<0.2	1156	19
Methyl cyclopentane	22	<0.2	164	17
Cyclohexane	24	<0.2	146	17
Heptanes	80	<0.2	433	19
Methyl cyclohexane	24	<0.2	175	17
Octanes	30	<0.1	280	19
Nonanes	11	<0.1	280	19
Decanes	6	<0.1	120	19
Undecanes	1	<0.1	20	19
Dodecanes	0.4	<0.1	2.6	19
Tridecanes	<0.1	<0.1	0.7	19
Tetradecanes	<0.1	<0.1	0.2	19
Aromatics:				
Benzene	7	<0.2	471	17
Toluene	6	<0.1	100	17
Ethylbenzene	0.3	<0.1	15	17
Xylenes	1	0.2	33	17
C3-benzenes	<0.1	<0.1	6	19
Naphthalenes	<0.1	<0.1	<1	19
PAHs	<0.02	<0.02	<0.02	19

Table 29. Test Results of Trace Natural Gas Constituents Sampling and Analysis (Sulfur Components)

	Median Value	Minimum Value	Maximum Value	Number of Values
Sulfur Components, ppmv:				
Hydrogen sulfide	<1	<0.02	6	19
Carbonyl sulfide	<0.02	<0.02	0.24	11
Carbon disulfide	<0.02	<0.02	0.02	11
Methyl mercaptan	<0.02	<0.02	0.15	19
Ethyl mercaptan	<0.02	<0.02	0.16	19
i-Propyl mercaptan	<0.02	<0.02	0.86	19
n-Propyl mercaptan	<0.02	<0.02	0.05	19
t-Butyl mercaptan	<0.02	<0.02	0.97	19
Dimethyl sulfide	<0.02	<0.02	0.5	19
Dimethyl disulfide	<0.02	<0.02	0.8	8
Methyl ethyl sulfide	<0.02	<0.02	0.06	11
Diethyl sulfide	<0.02	<0.02	0.05	11
Methyl ethyl disulfide	<0.02	<0.02	0.05	11
Diethyl disulfide	<0.02	<0.02	0.06	11
Methyl i-propyl disulfide	<0.02	<0.02	0.04	11
Ethyl i-propyl disulfide	<0.02	<0.02	0.12	11
Ethyl n-propyl disulfide	<0.02	<0.02	0.03	11
i-Propyl n-propyl disulfide	<0.02	<0.02	0.09	11
Di-n-propyl disulfide	<0.02	<0.02	0.03	11
i-Propyl t-butyl disulfide	<0.02	<0.02	0.02	11
Ethyl t-butyl disulfide	<0.02	<0.02	0.03	11
Di-t-butyl disulfide	<0.02	<0.02	0.02	11
Thiophane	<0.02	<0.02	0.51	19
Di-t-butyl trisulfide	<0.02	<0.02	0.4	8
Other target compounds	<0.02	<0.02	<0.02	19
Other compounds	<0.02	<0.02	0.75	19

Note: Some pipeline sites sampled were not required to contain odorant due to their classification.

Table 30. Test Results of Trace Natural Gas Constituents Sampling and Analysis (Halocarbons, Nitrogen Compounds, Oxygenates, and Other Elements and Compounds)

	Median Value	Minimum Value	Maximum Value	Number of Values
Halocarbons, ppmv:				
35 target compounds	<0.1	<0.1	<0.1	17
PCBs	<0.01	<0.01	<0.01	17
Other compounds	<0.1	<0.1	<0.1	17
Nitrogen Compounds, ppmv:				
Ammonia	<4	<4	<4	17
17 target compounds	<0.5	<0.5	<0.5	17
Other compounds	<0.5	<0.5	<0.5	17
Oxygenates, ppmv:				
Methanol	8	<1	92	19
Acetaldehyde	<1	<1	<1	4
Acetone	<1	<1	24	19
Formaldehyde	<1	<1	<1	19
Other 14 target compounds	<1	<1	<1	19
Other compounds	<1	<1	6	19
Other Elements				
Total Arsenic, ug/m^3	<5	<2	4	19
Total Mercury, ug/m^3	<0.2	<0.01	0.02	19

Containers used for testing odor fade consisted of sections of plastic and steel pipes and two inerted stainless steel sampling cylinders (see Table 31). Containers #1A and #1B are 2-inch NPS Schedule 40 steel pipes previously used for underground natural gas service. Containers #2A through #2K are unused 2-inch NPS Schedule 40 steel pipe purchased for the project. Representative containers are shown in Figure 3. Note the much higher level of corrosion in Containers #1A and #1B as seen in the left and middle photos compared to the unused steel pipe Container #2A in the right photo.

Containers #3A through #3O are unused 2-inch DriscoPlex 6500 PE 2406 polyethylene pipes.

Containers #4 and #5 are 304 stainless steel gas sampling cylinders that have been inerted with a silicon-containing coating on the interior of the cylinder (Sulfinert, Restek Corporation, Bellefonte, PA).[105] These two containers were designed to be used as “control reactors” for comparison with the results obtained with the pipes.

Table 31. Containers Used for the Static Testing

Container #	Container Type	Diameter and Length	Source	Volume, liter
1	Steel Pipe	2-inch x 1.0 ft.	Previously used for underground natural gas service	0.618
2	Steel Pipe	2-inch x 1.0 ft.	Unused, GTI stock	0.618
3	Polyethylene Pipe (DriscoPlex 6500 PE 2406)	2-inch x 1.0 ft.	Unused, GTI stock	0.618
4	304 Stainless Steel Gas Sampling Cylinder	3.14-inch x 0.91 ft	New, Sulfinert treated	1.00
5	304 Stainless Steel Gas Sampling Cylinder	3.14-inch x 0.91 ft	New, Sulfinert treated	1.00

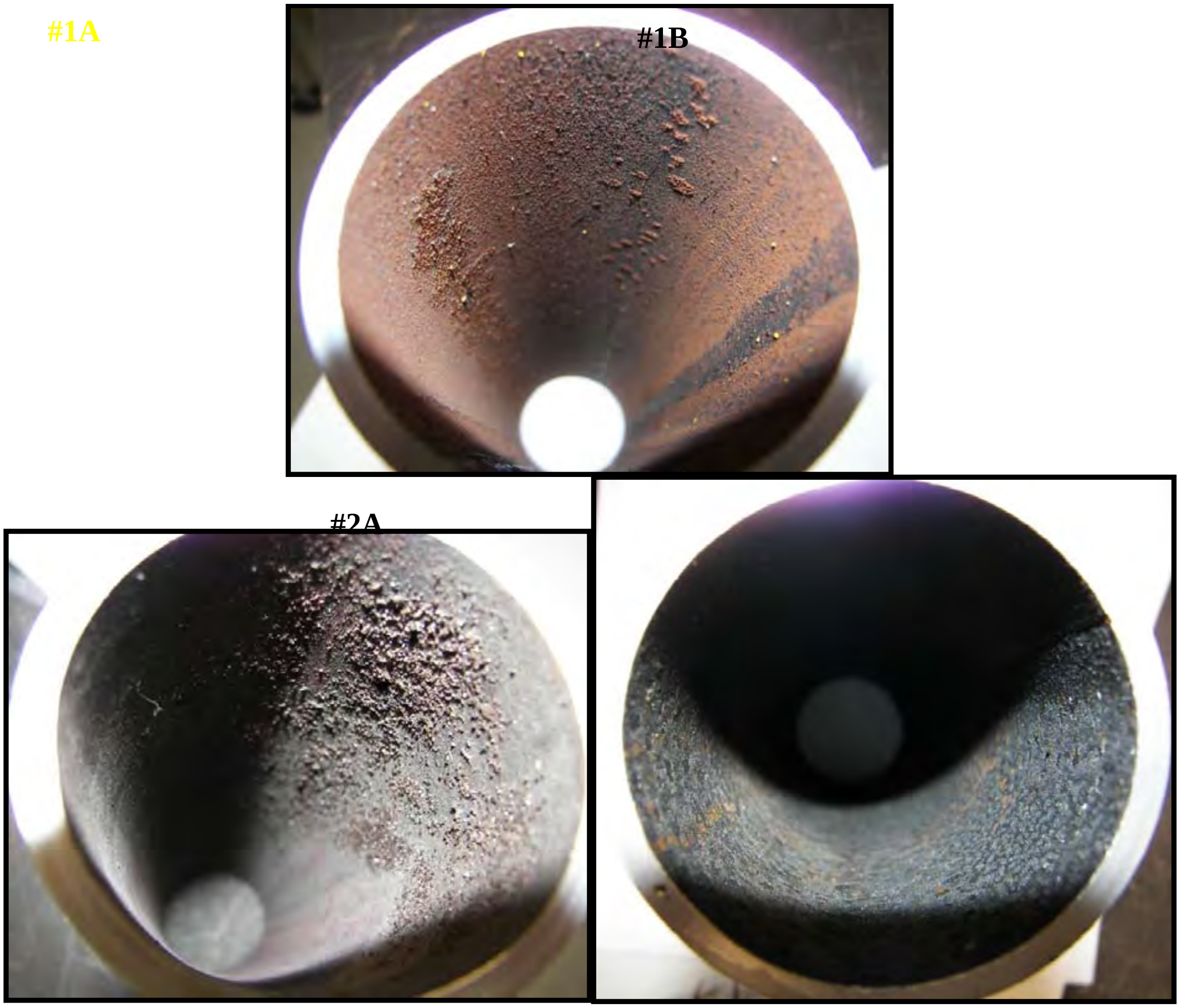


Figure 3. Steel Test Containers #1A, #1B and #2A with Differing Levels of Corrosion

The equipment setup used for the static testing is shown in Figure 4. The setup is configured for testing one-foot lengths of the two-inch NPS pipes using inerted stainless steel (316) flanges with captured o-rings for sealing the pipe ends. Longer pipe lengths could be accommodated for testing using typical (treated) steel pipe end caps in place of the flanges to seal the pipes.

Figure 4. Setup for Static Testing of the Test Pipes

The sequential steps of the procedures generally employed for the static testing are shown in Figure 5 and Figure 6. Briefly, the static test procedures involved repeatedly evacuating and filling the containers with 99.999% pure methane to remove as much as possible any remaining air/oxygen. The containers were then filled to 60 psig with the TBM-containing test gas from pressurized gas cylinders (Figure 7). Gas samples were withdrawn periodically from the containers for determination of the TBM concentration by gas chromatographic (GC) analyses. Gas volumes withdrawn from the pipe for GC analysis were in the microliter range to avoid disturbing equilibrium. Additional testing was performed using the same container by depressurizing and evacuating it as above and then refilling it with the TBM-containing test gas.

The first trace/contaminant compound to be tested, O_2, was added as a gas using a syringe to inject the compound into the container. MEA, methanol, water, and hexanes were added as liquids. This was accomplished via a septum-equipped valve connected to the container (Figure 8). The final test gas was a blend of methyl mercaptan (MM) in UHP methane. It was added using the same procedure as the TBM gas was added. In this instance, each gas (TBM and MM) were added in 30 psig aliquots to equal the 60 psig total.

The vapor phases were analyzed using gas chromatography with the appropriate detector for the compound being examined. The trace constituent analysis was performed using a flame ionization detector (FID). The odorant compounds were analyzed using a gas chromatograph that uses a pulsed flame photometric detector (PFPD) for the determination of low-level sulfur compounds. The GC is capable of detecting the compounds shown in Table 32, which include odorants and their possible reaction products.

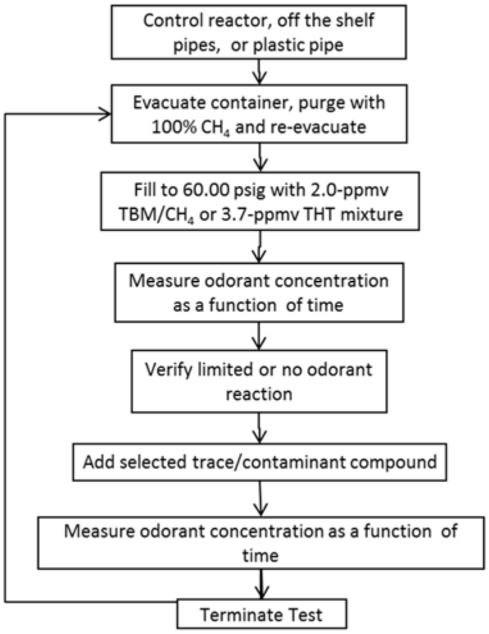


Figure 5. Scheme for Static Testing of Control Reactors and Plastic Pipe

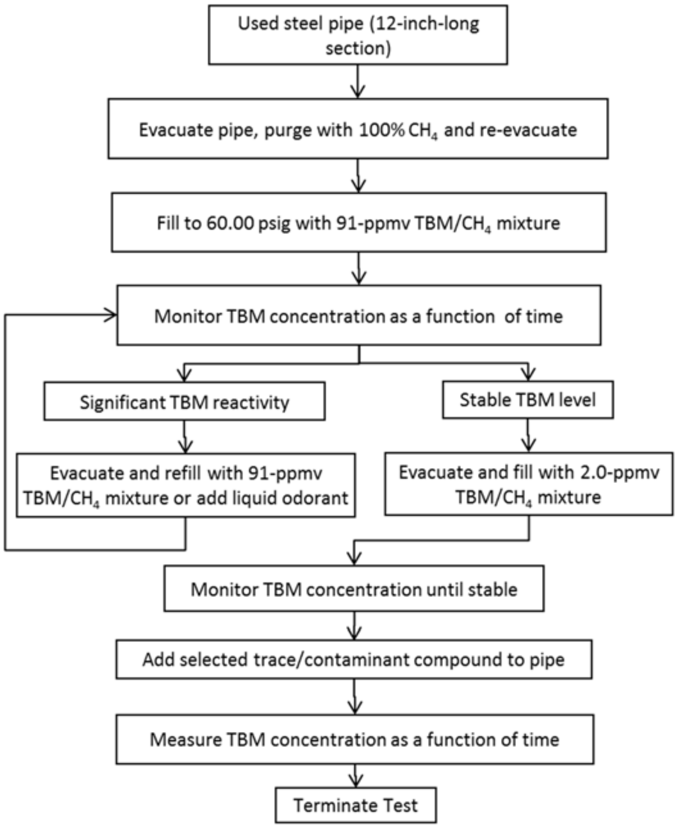


Figure 6. Scheme for Static Testing of Steel Pipes

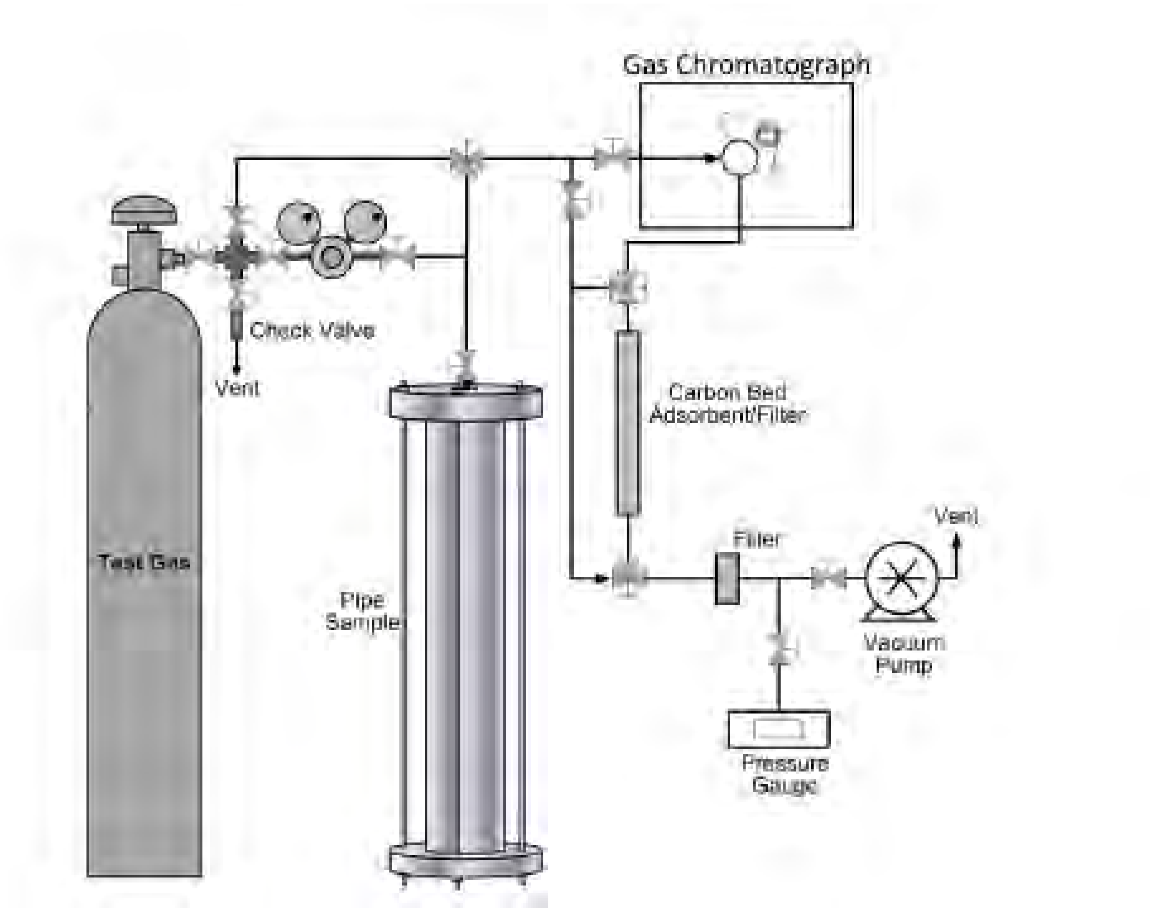


Figure 7. Setup for Trace Compound Addition from Pressurized Gas Cylinders

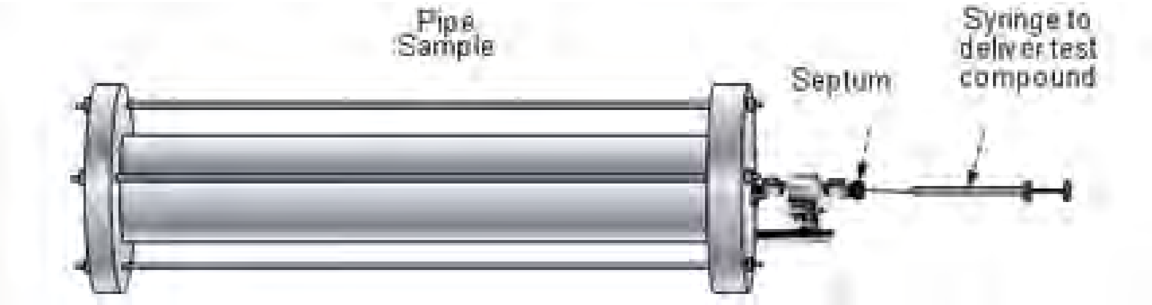


Figure 8. Setup for Trace Compound Addition using a Syringe

Table 32. Sulfur Compounds Detected

Compound	Compound
hydrogen sulfide	ethyl n-propyl disulfide
sulfur dioxide	ethyl t-butyl disulfide
carbonyl sulfide	di-i-propyl disulfide
carbon disulfide	i-propyl n-propyl disulfide
methyl mercaptan	di-n-propyl disulfide
ethyl mercaptan	i-propyl t-butyl disulfide
i-propyl mercaptan	n-propyl t-butyl disulfide
n-propyl mercaptan	di-t-butyl disulfide
t-butyl mercaptan	dimethyl trisulfide
dimethyl sulfide	diethyl trisulfide
methyl ethyl sulfide	di-t-butyl trisulfide
diethyl sulfide	thiophene
di-t-butyl sulfide	C1-thiophenes
dimethyl disulfide	C2-thiophenes
methyl ethyl disulfide	C3-thiophenes
methyl i-propyl disulfide	benzothiophene
diethyl disulfide	C1-benzothiophenes
methyl n-propyl disulfide	C2-benzothiophenes
methyl t-butyl disulfide	tetrahydrothiophene
ethyl i-propyl disulfide	

NIST traceable certified calibration standards of the odorant and trace compound gas mixtures in pressurized gas cylinders were prepared by a vendor or prepared in-house using traceable balances and pressure transducers.

The conditions performed for the static testing are given in Table 33. A preliminary test with one of the used steel pipe containers filled with the nominal 2 ppmv TBM test gas indicated complete degradation of the TBM concentration immediately upon filling. Because of this occurrence, it was decided to initially test the steel pipes (tests 1, 2 and 8) using higher concentrations of TBM, specifically 91 ppmv and 283 ppmv, instead of the nominal 2 ppmv TBM test gas.

Table 33. Static-Testing Conditions

Test #	Container #	Test Gas	Test Compounds
1	1A	91 ppmv TBM in balance CH_4 @ 60 psig	None (first fill)
2	2A	91 ppmv TBM in balance CH_4 @ 60 psig	None
3	3A	2 ppmv TBM in balance CH_4 @ 60 psig	None
4	4	2 ppmv TBM in balance CH_4 @ 60 psig	None
5	4	2 ppmv TBM in balance CH_4 @ 60 psig	300 ppmv O_2
6	4	2 ppmv TBM in balance CH_4 @ 60 psig	1000 ppmv O_2
7	4	2-ppmv TBM in balance CH_4 @ 60 psig	19 ppmv methanol
8	1B	91 & 283 ppmv TBM in balance CH_4 @ 60 psig	Liquid TBM
9	4	2 ppmv TBM in balance CH_4 @ 60 psig	152 ppmv methanol
10	5	2 ppmv TBM in balance CH_4 @ 60 psig	1000 ppmv hexanes
11	4	2 ppmv TBM in balance CH_4 @ 60 psig	60 ppmv MEA
12	4	2 ppmv TBM in balance CH_4 @ 60 psig	21 ppmv MEA
13	5	2 ppmv TBM in balance CH_4 @ 60 psig	141 ppmv H_2O
14	2B, 2C	2 ppmv TBM in balance CH_4 @ 60 psig	None, two temperatures
15	3B, 3C	4 ppmv THT in balance natural gas @ 60 psig	None, two temperatures
16	2D, 2E	4 ppmv THT in balance natural gas @ 60 psig	None, two temperatures
17	3D, 3E	2 ppmv TBM in balance CH_4 @ 60 psig	None, two temperatures
18	5	2 ppmv TBM in balance CH_4 @ 30 psig	2 ppmv MM in balance CH_4 @ 30 psig
19	2F, 2G	2 ppmv TBM in balance CH_4 @ 37½ psig plus 4 ppmv THT in balance natural gas @ 37½ psig	None, two temperatures

Test #	Container #	Test Gas	Test Compounds
20	3F, 3G	2 ppmv TBM in balance CH_4 @ 37½ psig plus 4 ppmv THT in balance natural gas @ 37½ psig	None, two temperatures
21	3H, 3I, 3J, 3K	2 ppmv TBM in balance CH_4 @ 60 psig	None, four temperatures
22	3L, 3M, 3N, 3O	4 ppmv THT in balance natural gas @ 60 psig	None, four temperatures
23	2H, 2I, 2J, 2K	2 ppmv TBM in balance CH_4 @ 60 psig	Water at 1300 ppmv, four temperatures

Test #1 Results (91 ppmv TBM in CH_4 in Used Pipe Container #1A)

The TBM concentration decreased rapidly in the used pipe container #1A (Figure 9) within a few hours after the first fill with the 91 ppmv TBM test gas and after each succeeding fill to below 0.1 ppmv (in all but the first fill where it was 0.4 ppmv). As the used pipe was still highly reactive to the TBM, Test #8 was designed to add liquid TBM in order to “quench” its reactivity.

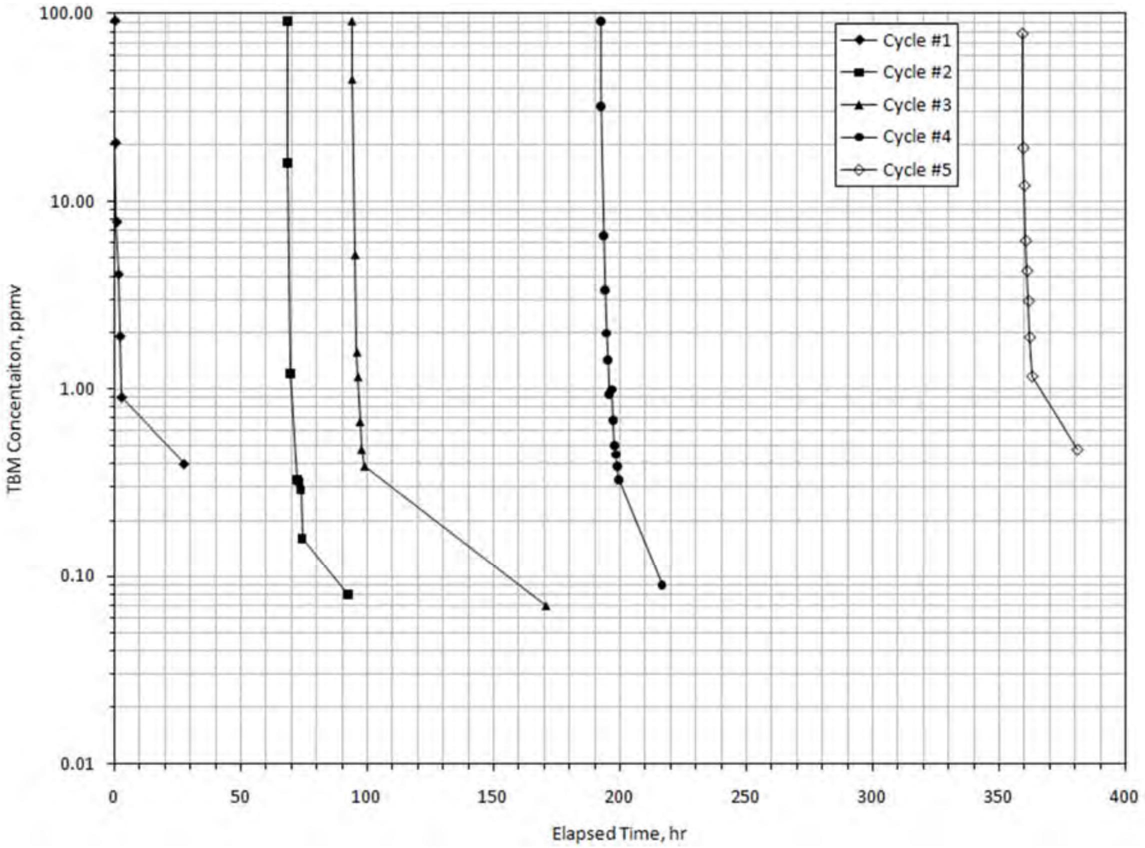


Figure 9. TBM Reactivity in Container #1A (previously used 2-in NPS steel pipe) – Test #1

The fading data appear to fit to a power law function: $conc = a(time)^{b}$. The a and b constants vary between the five different runs but are generally in the same range. This data along with the R^2 (coefficient of determination) evaluation of the curve fit is shown in Table 34. (R^2 is a statistic that gives some information about the goodness of fit of a model or equation. The closer it is to unity (1) the better the fit is.)

Table 34. Curve Fit Parameters of Test #1

Cycle #	Value of "a" Constant	Value of "b" Constant	R^2 Evaluation of Curve Fit
1	147	-0.85	0.90
2	93	-1.01	0.98
3	183	-1.00	0.94
4	335	-1.10	0.95
5	172	-0.80	0.96

Test #2 Results (91 ppmv TBM in CH_4 in Off-the-Shelf Pipe Container #2A)

Test #2 was performed with the unused off-the-shelf steel pipe (Container #2A) using the 91 ppmv TBM in CH_4 test gas. The TBM concentration decreased rapidly in 9 minutes, 4 hours, and 20 minutes, respectively, in cycles 1-3 to 59, 52 and 65 ppmv (Figure 10). The TBM concentrations then leveled out at average values of 50, 62 and 64 ppmv in cycles 1-3, respectively. It appears that in all three fill cycles that the TBM faded immediately, but came to an equilibrium concentration quickly.

The data fit is likely a power curve also, but it is difficult to make a good assessment of the equation constants when the TBM concentration faded so quickly. This is due to lack of data points just after the gas was added. Table 35 is an attempt to calculate the curve fit parameters of a power curve. There were an insufficient number of early data points in cycle 3 to make any calculation.

After the rapid initial decline, the data show low TBM loss rates (from a linear least square regression of the TBM concentration versus time data after the initial decline) of 0.33 and 0.27 ppmv/100 hours, respectively, indicating that the TBM concentration had stabilized at an average of 59 ppmv.

As a result, this pipe was evacuated and refilled with the nominal 2 ppmv TBM in CH_4 test gas mixture (to 60.0 psig total) in cycle 4 to determine the stability of this lower TBM level with time. As shown in the lower plot in Figure 10, the TBM rapidly declined from initially 2.0 to 1.75 ppmv after 0.5 hours, declining further to 1.22 ppmv in ~2200 hours at which time the test was terminated. This resulted in a calculated TBM loss rate of only ~0.02 ppm/100 hours, significantly less than the 0.27 value obtained in cycle 3, indicating the effect of pre-conditioning on reducing TBM reactivity.

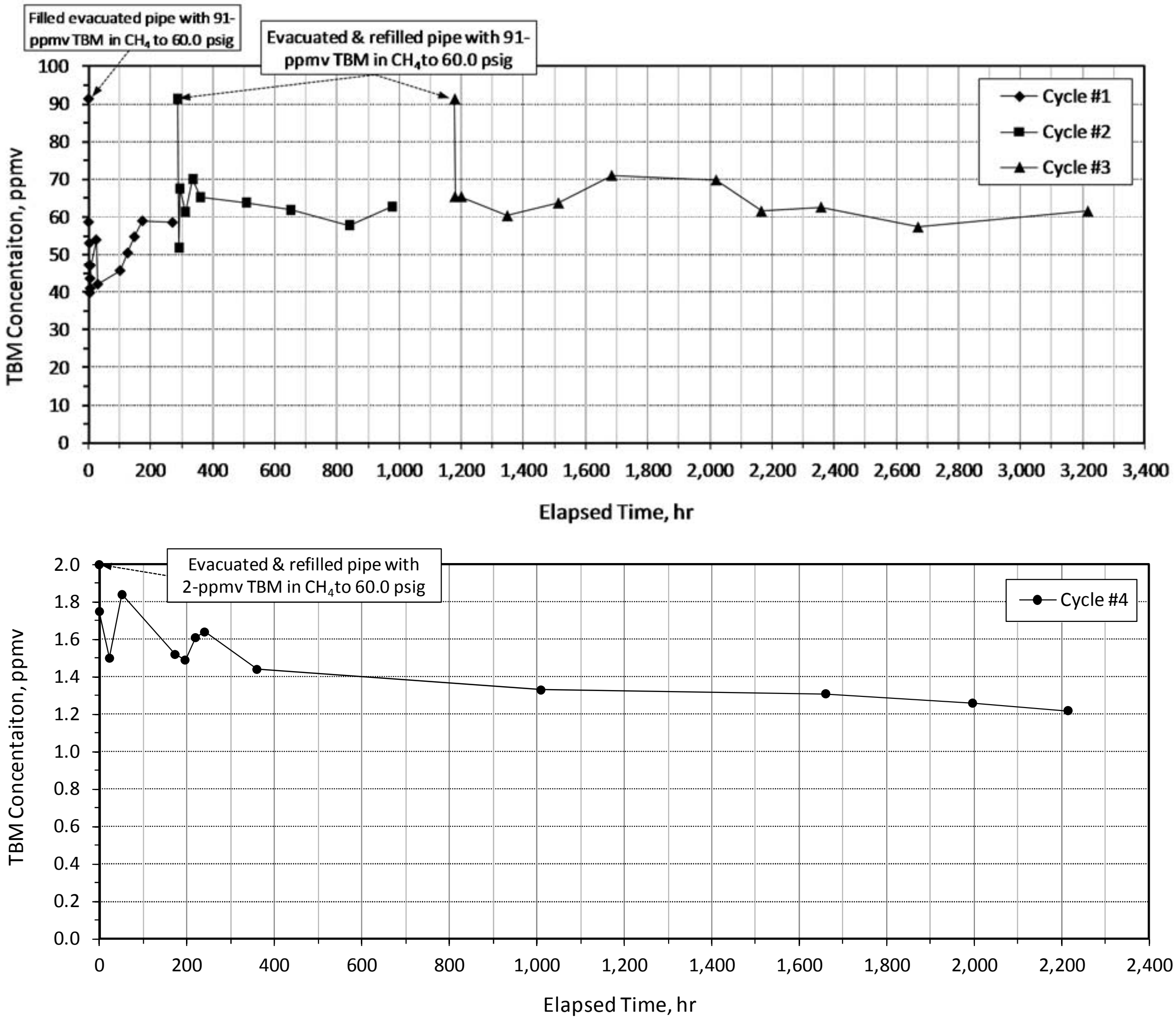


Figure 10. TBM Reactivity in Container #2A (Off-the-Shelf 2-in Steel Pipe) – Test #2
Top: 91 ppmv TBM; Bottom: 2 ppmv TBM

Table 35. Curve Fit Parameters of Test #2

Cycle #	Value of "a" Constant	Value of "b" Constant	R^2 Evaluation of Curve Fit
1	59	-0.032	0.83
2	69	-0.022	0.82

Test #3 Results (2 ppmv TBM in CH_4 in Plastic Container #3A)

Test #3 was performed with an unused plastic pipe (Container #3A). Two test cycles were performed. In cycle #1, as shown in the left side plot in Figure 11, the TBM concentration slowly decreased from an initial nominal 2 ppmv to 0.24 ppmv over the 2400-hour duration first cycle. This corresponds to an initial TBM loss rate of ~0.1 ppmv/100 hours.

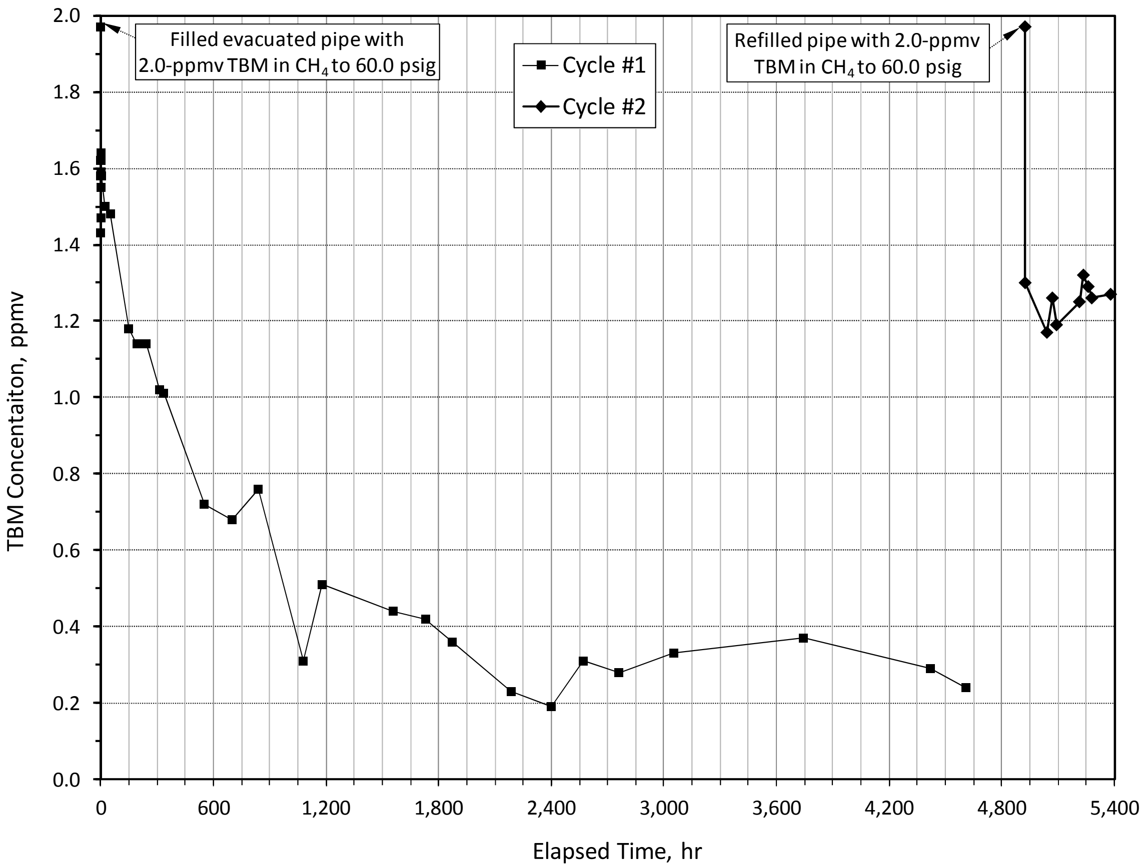


Figure 11. TBM Reactivity in Container #3A (off-the-shelf 2-inch NPS plastic pipe) after Two Cycles – Test #3

The curve fit to the cycle #1 data was further investigated using a non-linear least squares fitting program, and the best fit found was similar to a second order kinetic curve with the following equation:

$$\text{Concentration} = \frac{1}{\frac{1}{a}+(b*time)} \qquad \text{where a = 1.576 and b = 0.0000198}$$

Figure 12 shows the cycle #1 data fitted to the curve, with a coefficient of determination of 0.991.

The curve fit is different because the phenomena occurring in this test sequence is different than in the testing with steel pipe. No iron oxide active sites are present; the reason for odor fade is absorption and/or adsorption.

The pipe was filled a second time (cycle #2) with the nominal 2 ppmv TBM test gas to determine its stability with time. As indicated in the right side plot in Figure 11, the TBM concentration initially declined rapidly in cycle 2 to 1.30 ppmv but remained steady at an average of about 1.26 ppmv over the next 455 hours. The TBM loss rate was calculated to be nearly zero and is significantly less than the initial TBM loss rate of 0.16 ppmv/100 hours obtained in same time period in the first cycle, suggesting that the pipe was conditioned by its first exposure to TBM.

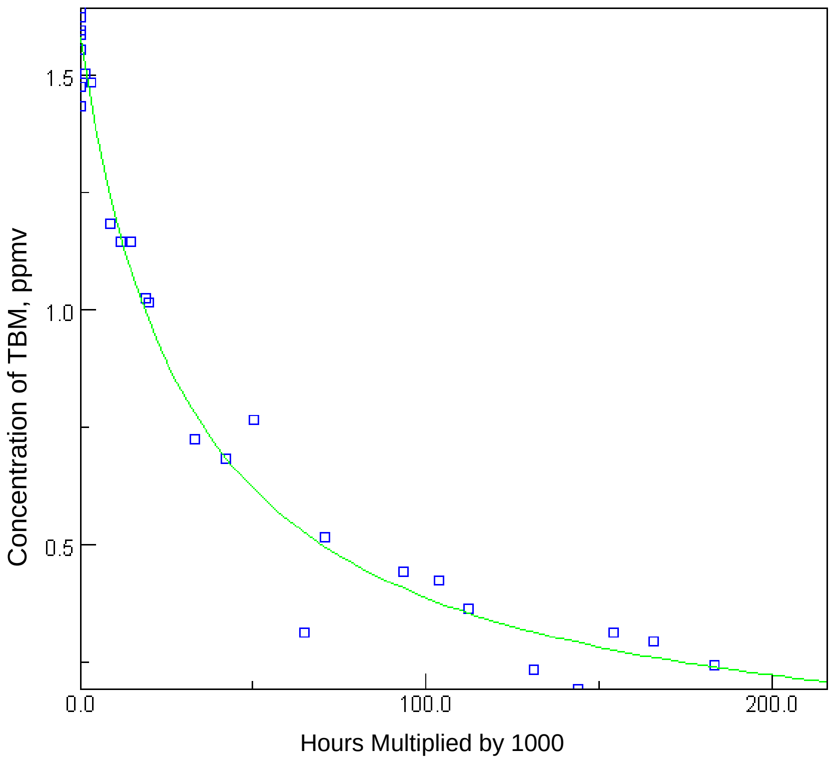


Figure 12. Curve Fit for Data from Test #3

Test #4 Results (2 ppmv TBM in CH_4 in Inerted Container #4)

Test #4 was conducted to determine the stability of TBM in the Sulfinert-treated control reactor (Container #4). It was initially filled with the nominal 2 ppmv TBM in CH_4 test gas mixture to a total pressure of 60 psig. The TBM concentration in the reactor remained relatively stable between 1.6-2.0 ppmv over the 190-hour test period (Figure 13).

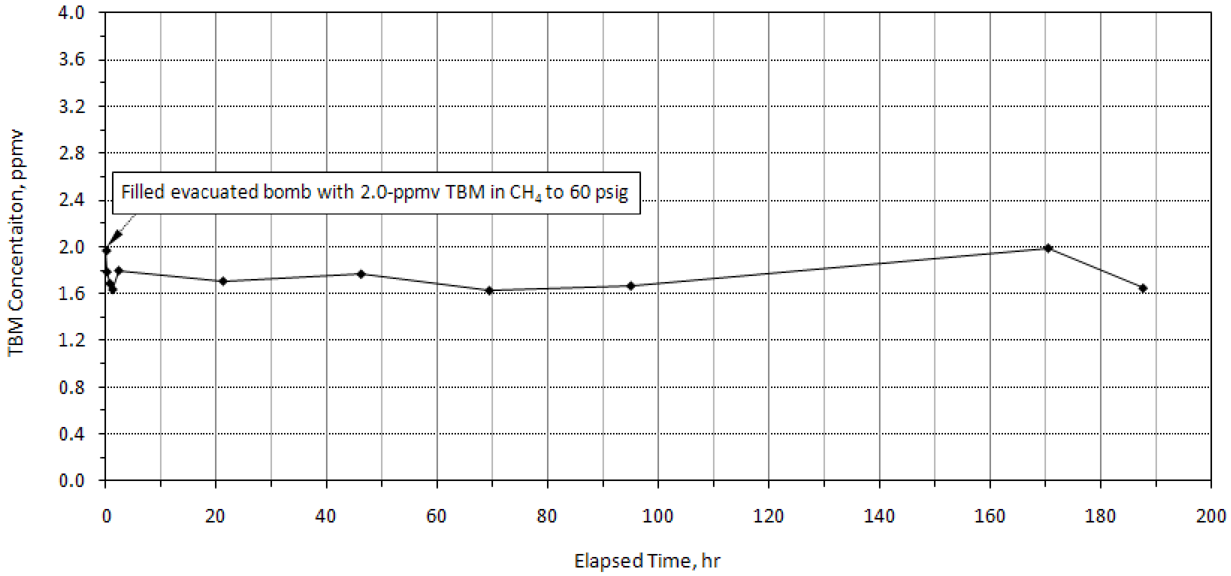


Figure 13. TBM Reactivity in the Control Reactor – Test #4 without Added Constituents

After this test, the reactor was evacuated and refilled with the test gas. The TBM level was again observed to be fairly stable for the first 140 hours after the second filling, and in both cases showing greater stability than the plastic pipe. As long-term stability of the TBM was demonstrated, it was decided to use it to reliably investigate the possible effects of the trace/contaminant TBM reactivity. At this point a trace amount of oxygen was added to Container #4 for Test #5.

The data from Test #4 were used for some of the statistical analyses comparison ($P<0.05$ or 95% confidence limit) of subsequent odor fade studies using added trace constituents for Tests #5 through #12, also performed in the inerted cylinder control reactors. This analysis will show if the added constituent had a statistically significant effect on the TBM reactivity. The baseline data are in Table 36. Because some issues were seen with the TBM analysis in Test #13, its baseline test was performed separately.

Table 36. Statistical Baseline Data for Test #4

Statistic	Baseline Value
# of data points	10
t-statistic	2.26
average	1.73
standard deviation	0.11
95% Confidence Limit	0.08
Upper Confidence Limit	1.81
Lower Confidence Limit	1.66

Tests #5 and #6 Results (2 ppmv TBM in CH_4 with Oxygen in Inerted Container #4)

Tests #5 and #6 were conducted in a control reactor (Container #4) to determine the stability of the nominal 2 ppmv TBM in CH_4 gas mixture with oxygen added at levels of 300 ppmv and 1000 ppmv O_2, respectively. The stability of the TBM in this control reactor was verified for 140 hours before adding the O_2, as mentioned in the discussion of Test #4.

At 70 hours after the first and 92 hours after the second injection of O_2, the TBM concentration was still steady at 1.7 ppmv, indicating no significant effect of the O_2 on TBM reactivity (Figure 14). Additionally, a gas analysis was conducted twenty-four hours after the second O_2 injection that indicated no decrease in the reactor O_2 concentration. Similar results were obtained in other studies[19,46] with mercaptans and O_2 using various container materials.

Statistical data ($P<0.05$ or 95% confidence limit) are presented in Table 37.

One way to determine significance is to calculate the upper (UCL) and lower (LCL) confidence limits of the data sets. If the range of values represented by the UCL and LCL of the baseline test overlap with the UCL and LCL of the tests with added oxygen, there is no difference between the data sets. Table 37 shows that there is overlap, meaning that the interval of 1.72-1.64 has a range in common with the interval of 1.81-1.66. This is also demonstrated graphically in Figure 15.

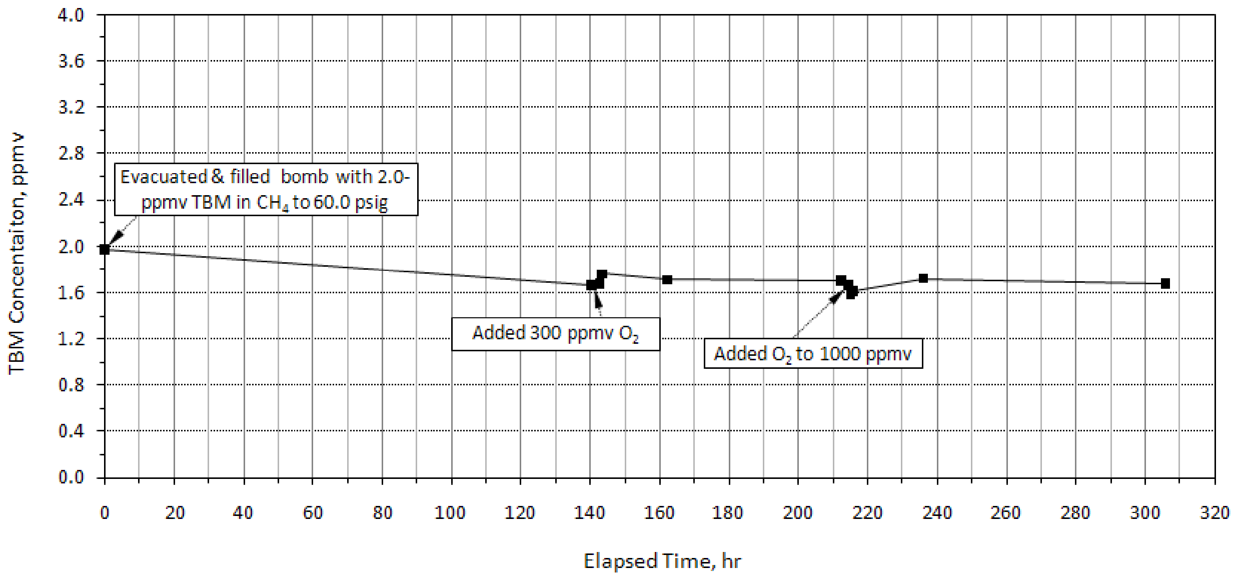


Figure 14. TBM Reactivity in the Control Reactor – Tests #5 and #6 with 300- and 1000-ppmv O_2 Added

Table 37. Statistical Data for Test #5 and #6 (Combined)

Statistic	Value for Test #5/#6	Baseline Value
# of data points	9	10
t-statistic	2.31	2.26
average	1.68	1.73
standard deviation	0.055	0.11
95% Confidence Limit	0.04	0.08
Upper Confidence Limit	1.72	1.81
Lower Confidence Limit	1.64	1.66

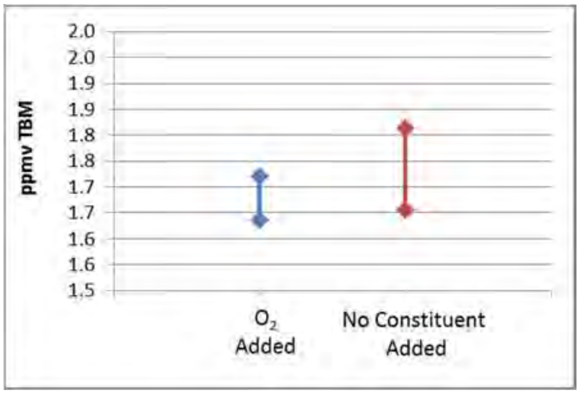


Figure 15. Graphical Demonstration of UCL and LCL for Baseline and Tests #5 and #6 with 300- and 1000-ppmv O_2 Added

When making a comparison test between two unpaired means, the null hypothesis is stated as "there is no statistical difference between the two sets of data". Assuming that this is true, statistical theory is used to calculate the probability that the difference is due to random error and not significant. Since the analyses were performed on the same instrument, standard deviations are assumed to be similar, so a pooled standard deviation is calculated. From the pooled standard deviation, a t statistic (t experimental) is calculated and compared to the t statistic for the total number of degrees of freedom (t critical). If t experimental is greater than t critical, the null hypothesis is rejected and there is a significant difference between the two sets of data. This procedure is more rigorous than the graphical method. Table 38 shows the calculated data. The null hypothesis is not rejected because t experimental is less than t critical. There is no statistical difference in the data. O_2 had no effect on odor fade at 1000 ppmv.

Table 38. Comparison of Test #5 and #6 (Combined) with the Baseline Test

Statistic	Pooled Value for Test #5/#6
pooled standard deviation	0.088
t experimental	1.39
t critical	2.11
Is t experimental > t critical?	no

Test #7 Results (2 ppmv TBM in CH_4 with Methanol in Inerted Container #4)

Test #7 was conducted in the control reactor (container #4) after it was depressurized, evacuated and refilled with the nominal 2 ppmv TBM in CH_4 test gas (Figure 16) to a total pressure of 60.0 psig. At 18 hours after filling, the TBM level in the reactor was determined to be 1.58 ppmv. At 48 hours into the test, liquid methanol was injected into the reactor via the attached septum at a level of 19 ppmv. During the next 377 hours the TBM concentration in the reactor declined to only 1.42 ppmv and the test was terminated.

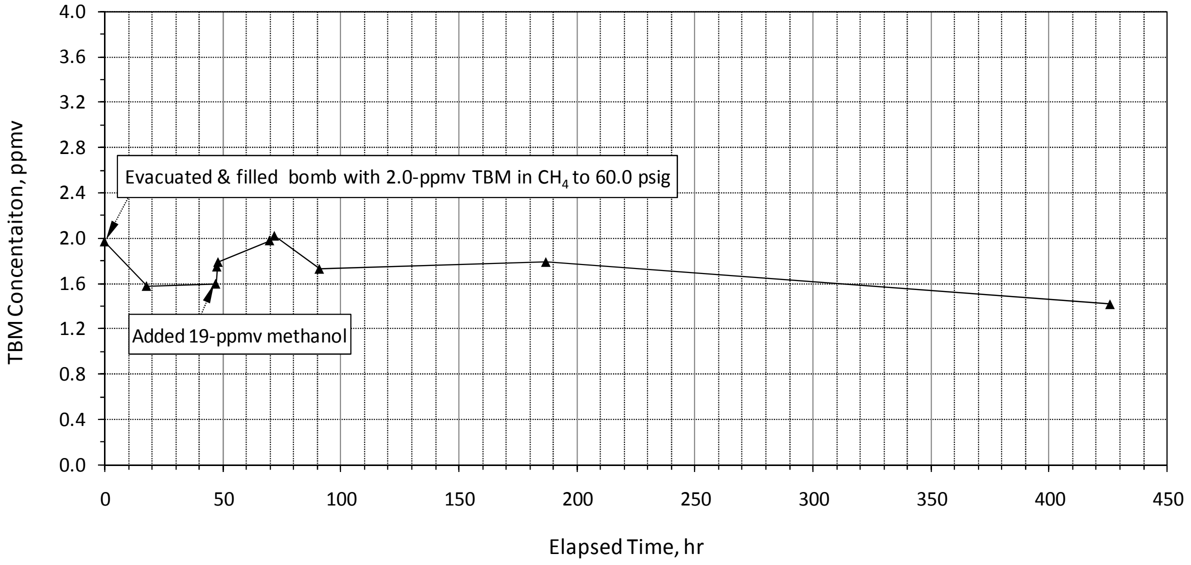


Figure 16. TBM Reactivity in the Control Reactor – Test #7 with 19 ppmv Methanol Added

Statistical data (P<0.05 or 95% confidence limit) are presented in Table 39 and Table 40. Table 39 shows that there is overlap in the UCL and LCL for the baseline and the experimental data. This is also demonstrated graphically in Figure 17. Table 40 shows that the null hypothesis is not rejected because t experimental is less than t critical. There is no statistical difference in the data. Methanol at 19 ppmv had no effect on odor fade.

Table 39. Statistical Data for Test #7

Statistic	Value for Test #7	Baseline Value
# of data points	8	10
t-statistic	2.36	2.26
average	1.75	1.73
standard deviation	0.21	0.11
95% Confidence Limit	0.17	0.08
Upper Confidence Limit	1.92	1.81
Lower Confidence Limit	1.58	1.66

Table 40. Comparison of Test #7 with the Baseline Test

Statistic	Pooled Value for Test #7
pooled standard deviation	0.159
t experimental	0.196
t critical	2.12
Is t experimental > t critical?	no

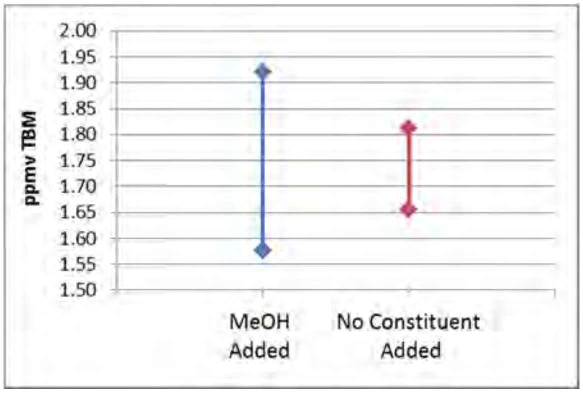


Figure 17. Graphical Demonstration of UCL and LCL for Baseline and Test #7 with 19 ppmv Methanol Added

Test #9 Results (2 ppmv TBM in CH_4 with Methanol in Inerted Container #4)

(Note that results from Test #9 are presented here before Test #8 in order to present the methanol information in close proximity to Test #7.) Test #9 was conducted using a control reactor to determine the effect of methanol at a higher concentration of 152 ppmv on the reactivity of TBM (Figure 18). After heating and evacuating the reactor, methanol was injected and the reactor filled to 60.0 psig with the nominal 2 ppmv TBM in CH_4 test gas mixture. The reactor was sampled about 4 minutes after adding the TBM and the results indicated that the TBM concentration had declined to 1.61 ppmv. The TBM concentration remained fairly steady over the next 700 hours, however, declining to only 1.57 ppmv at which time the test was terminated.

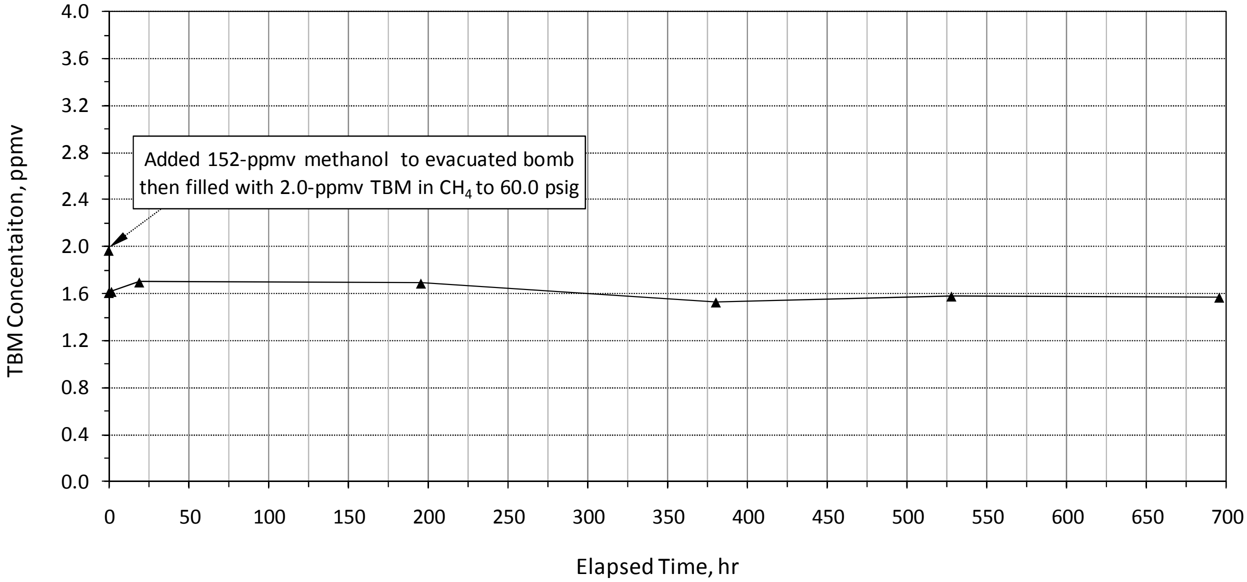


Figure 18. TBM Reactivity in the Control Reactor – Test #9 with 150 ppmv Methanol Added

Statistical data (P<0.05 or 95% confidence limit) are presented in Table 41 and Table 42. Table 41 shows that there is very little overlap in the UCL and LCL for the baseline and the experimental data. This is also demonstrated graphically in Figure 19. Table 42 shows that the null hypothesis is rejected because t experimental is greater than t critical, indicating that there is a statistical difference in the data. Because the graphical demonstration shows a slight overlap, and the statistical evaluation shows no effect, the evaluation is inconclusive. However, it appears that methanol at higher concentrations may have an effect on odor fade.

Table 41. Statistical Data for Test #9

Statistic	Value for Test #9	Baseline Value
# of data points	7	10
t-statistic	2.45	2.26
average	1.61	1.73
standard deviation	0.062	0.11
95% Confidence Limit	0.058	0.08
Upper Confidence Limit	1.67	1.81
Lower Confidence Limit	1.56	1.66

Table 42. Comparison of Test #9 with the Baseline Test

Statistic	Pooled Value for Test #9
pooled standard deviation	0.0935
t experimental	2.60
t critical	2.13
Is t experimental > t critical?	yes

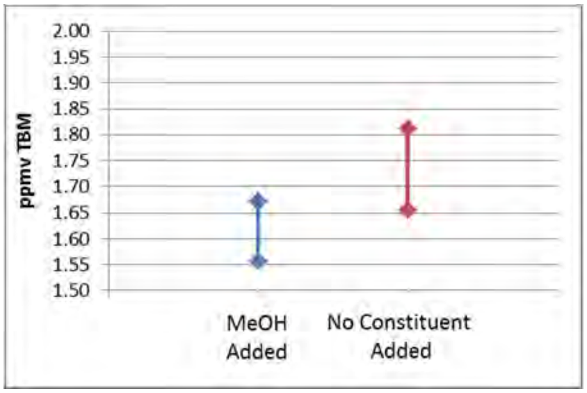


Figure 19. Graphical Demonstration of UCL and LCL for Baseline and Test #9 with 150 ppmv Methanol Added

Test #8 Results (91 and 283 ppmv TBM in CH_4 Methane using Liquid Odorant in Used Pipe Container #1B)

An objective of Test #8 was to determine the quantity of TBM required to “quench” the reactivity of a used, rusted pipe. A new one-foot section of steel pipe (Container #1B) cut from the same batch as Container #1A (used in Test #1 as reported previously) was used for this test.

An initial cycle (#0 in Figure 20) was conducted by filling the pipe (Container #1B) to 60.0 psig with the 91 ppmv TBM in CH_4 test gas and monitoring the TBM concentration with time. The pipe was highly reactive to the TBM as indicated by the rapid initial decrease from 91 to 33 ppmv in ~30 minutes and to <0.1 ppmv in ~24 hours (Figure 20). Because the gas phase concentration faded so quickly, it was decided to inject liquid TBM into the pipe (instead of using a standard gas) at 68 hours (cycle 1) into the test.

The amount of odorant to use was estimated from two different sources. Odorant application rate data used for pipeline conditioning that were available in the literature were shown previously (Table 10 and survey results). Also, in a private communication with a pipeline company, an odorant application rate of 0.25 milliliter 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 of thickness 0.254 micron. If applied to Container #1B, this rate would correspond to adding about 13 microliter of liquid TBM to the pipe. For the testing here, it was decided to initially use approximately 1/4th (equivalent to 283 ppmv TBM) of the total above odorant application rate, per injection or cycle, to prevent over saturation of the inner pipe wall with the TBM and to study the impact of several iterations.

After the first injection the TBM concentration in the pipe declined to 4 ppmv in 30 hours and to 1.3 ppmv 97 hours. Di-tertiary butyl disulfide (DTBDS) was first detected in the gas at a level of ~2 ppmv about 30 hours after injection.

DTBDS is an oxidation product of TBM, the formation of which was previously ascribed to the catalytic effect of the pipe surface oxidation products, usually iron oxides. This was described in the first quarterly report for this project. It reportedly lacks the characteristic odor of mercaptan.

After the TBM declined to ~1 ppmv in cycle 1, liquid TBM was injected into the pipe for the second time at 168 hours and the TBM monitored with time (cycle 2, Figure 20). The TBM concentration in the pipe declined to ~8 ppmv after 48 hours and to 3 ppmv after 384 hours. DTBDS was again detected in the gas at a slightly higher level of ~2-4 ppmv.

At 555 hours into the test and after the TBM concentration in cycle 2 had declined to ~3 ppmv, liquid TBM was injected for a third time into the pipe and the TBM monitored with time (cycle 3, Figure 20). As is the previous cycles, the TBM concentration rapidly declined but at a slower overall rate, reaching ~7 ppmv in 478 hours after the TBM injection. Higher levels of DTBDS in the range ~51 ppmv (approaching the concentration of the TBM) were detected in this cycle but also declined along with the TBM over time.

At ~1060 hours into the test and after the TBM declined to ~7 ppmv in cycle 3, liquid TBM was injected into the pipe for a fourth time and the TBM monitored with time (cycle 4, Figure 20). The TBM concentration declined to ~6 ppmv in about 550 hours after injection of the TBM, which is similar to the overall decline rate in cycle 3.

At ~3434 hours into the test and after the TBM had declined to ~0.1 ppmv (14 ppmv DTBDS) in cycle 4, liquid TBM was injected into the pipe for a fifth time and the TBM monitored with time (cycle 5, Figure 20). The TBM concentration initially declined from 283 ppmv injected to only ~200 ppmv (41 ppmv DTBDS) at about one hour after injection, which is a slower rate of decrease than observed in earlier cycles. However, the TBM decreased to only 11.8 ppmv (10 ppmv DTBDS) and then to 3.6 ppmv (no DTBDS detected, 8-ppmv C2 thiophenes) after 290 and 455 hours, respectively.

At ~4400 hours into the test and after the TBM had declined to ~0.1 ppmv in 811 hours following the previous injection of TBM in cycle 5, liquid TBM was again injected into the pipe and the TBM monitored with time (cycle 6, Figure 20). The TBM concentration declined from the 283 ppmv injected to ~8 ppmv (plus 20 ppmv DTBDS) in ~500 hours after injection and then to only 0.10 ppmv (plus 0.41 ppmv DTBDS), over the next 1000 hours, indicating that the pipe had not yet been saturated.

Liquid TBM was injected into the pipe for a seventh time (cycle 7, Figure 20) at ~5550 hours after the TBM had declined to 0.10 ppmv in cycle 6. The TBM concentration declined from 283 ppmv initially injected to ~7 ppmv (plus 84-ppmv DTBDS) in ~330 hours and remained at about that level during the next ~240 hours.

The seven iterations of data were plotted to the same power law function previously used. In addition, the rate loss for the first few data points of each cycle was calculated. See Table 43.

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.

This confirmed field data from four case studies of pre-odorization/pickling. The field data indicate that by using the technique of injection of highly odorized gas, (TBM or TBM/IPM and MES blends), 0.2 to 0.4 mL/ft^2 of odorant addition was required to achieve full conditioning. Nearly double the odorant addition rate was required when using a continuous liquid addition technique. The odorant addition rate was significantly lower (0.05 mL/ft2) when using THT as the odorant, due to its known lower reactivity. The anecdotal application of 0.25 milliliter per square foot of internal pipe surface area is reasonable.

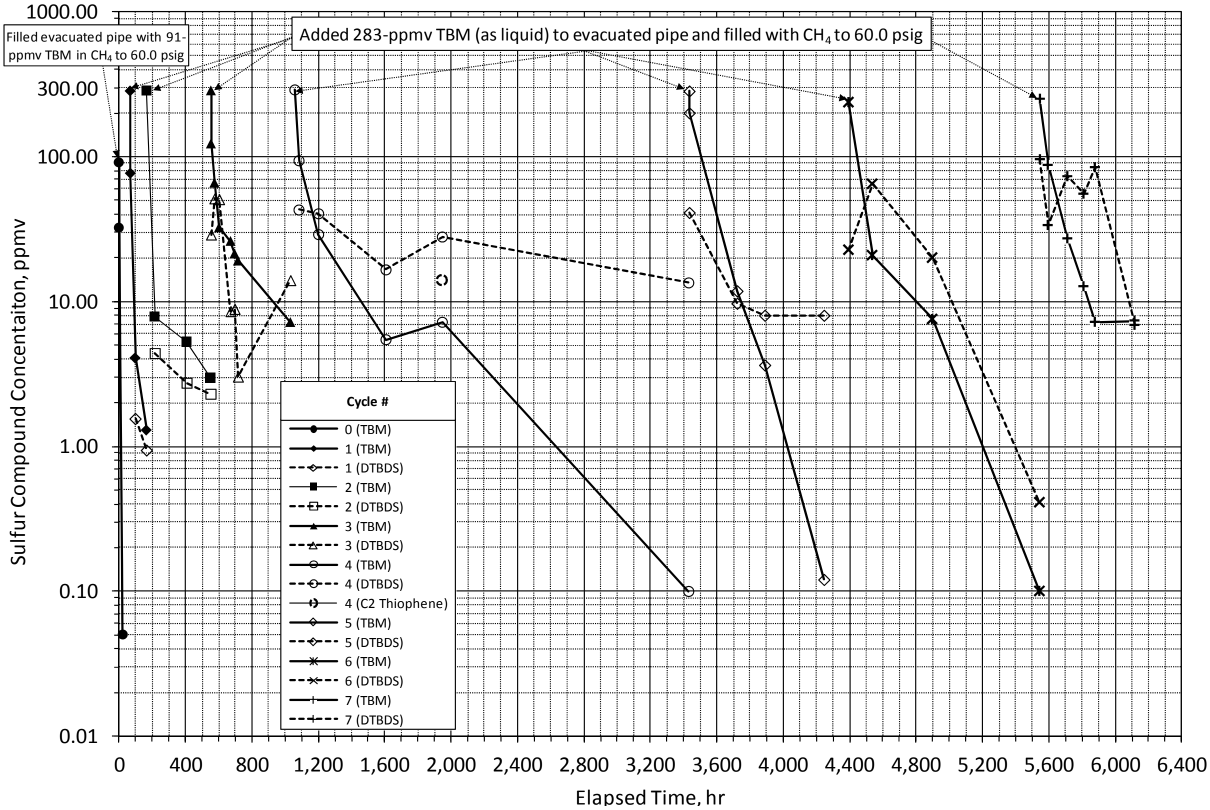


Figure 20. TBM Reactivity in Container #1B (Used 2-inch Steel Pipe) – Test #8, TBM and Di-TBDS Concentration with Time

Table 43. Curve Fit Parameters and Calculated Rates for Test #8

Cycle	Value of “a” Constant	Value of “b” Constant	R^2 Evaluation of Curve Fit	Initial Rate Loss of TBM, ppmv/hour
1	5	-0.90	1.00	150
2				137
3	36	-0.33	0.82	158
4	201	-1.31	0.80	33
5	17	-0.79	0.72	19
6	24	-0.84	0.71	40
7	71	-0.87	0.78	34

Test #10 Results (2 ppmv TBM in CH_4 with Hexanes in Inerted Container #5)

Test #10 (Figure 21) used a new Sulfinert-treated steel control reactor, (container #5) to determine the effect of hexane (actually a mixture of isomers) on TBM reactivity/loss. In this test the equivalent of ~1000-ppmv hexanes was injected as liquid into the evacuated container and the container was pressurized to 60.0 psig with the nominal 2 ppmv TBM in CH_4 test gas mixture. A gas analysis indicated a slight drop in TBM concentration to 1.66 ppmv after ~100 hours, which remained at about that level up to the end of the test at 2800 hours.

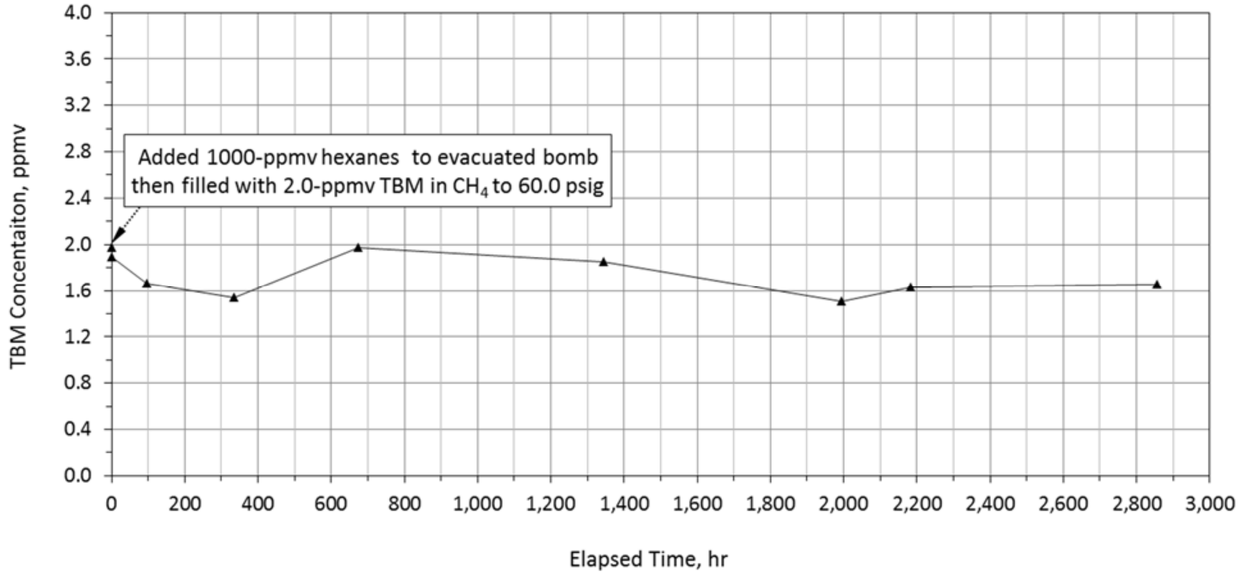


Figure 21. TBM Reactivity in the Control Reactor – Test #10 with 1000 ppmv Hexanes Added

Statistical data ($P<0.05$ or 95% confidence limit) are presented in Table 44 and Table 45. Table 44 shows that there is overlap in the UCL and LCL for the baseline and the experimental data. This is also demonstrated graphically in Figure 22. Table 45 shows that the null hypothesis is not rejected because t experimental is less than t critical, indicating that there is no statistical difference in the two sets of data. It can be concluded that hexanes at 1000-ppmv did not result in odor fade.

Table 44. Statistical Data for Test #10

Statistic	Value for Test #10	Baseline Value
# of data points	8	10
t-statistic	2.36	2.26
average	1.71	1.73
standard deviation	0.17	0.11
95% Confidence Limit	0.14	0.08
Upper Confidence Limit	1.85	1.81
Lower Confidence Limit	1.57	1.66

Table 45. Comparison of Test #10 with the Baseline Test #4

Statistic	Pooled Value for Test #10
pooled standard deviation	0.139
t experimental	0.326
t critical	2.12
Is t experimental > t critical?	no

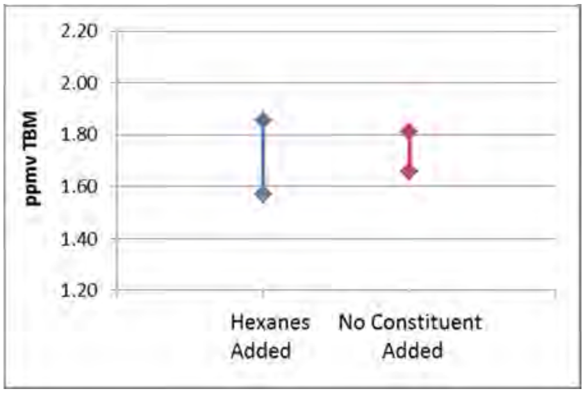


Figure 22. Graphical Demonstration of UCL and LCL for Baseline and Test #10 with 1000 ppmv Hexanes Added

Test #11 Results (2 ppmv TBM in CH_4 with MEA in Inerted Container #4)

Test #11 used a Sulfinert-treated steel sample control reactor (Container #4) to determine the effect of MEA on TBM reactivity/loss. In this test the equivalent of ~60 ppmv MEA was injected as liquid into the evacuated cylinder and the cylinder was pressurized to 60.0 psig with the nominal 2-ppmv TBM in CH_4 test gas mixture. An analysis of the gas in the cylinder after about one hour (Figure 23) indicated a rapid decline of the TBM concentration to 1.35 ppmv, which declined further to 1.21 ppmv over the next ~1440 hours, at which point the test was terminated.

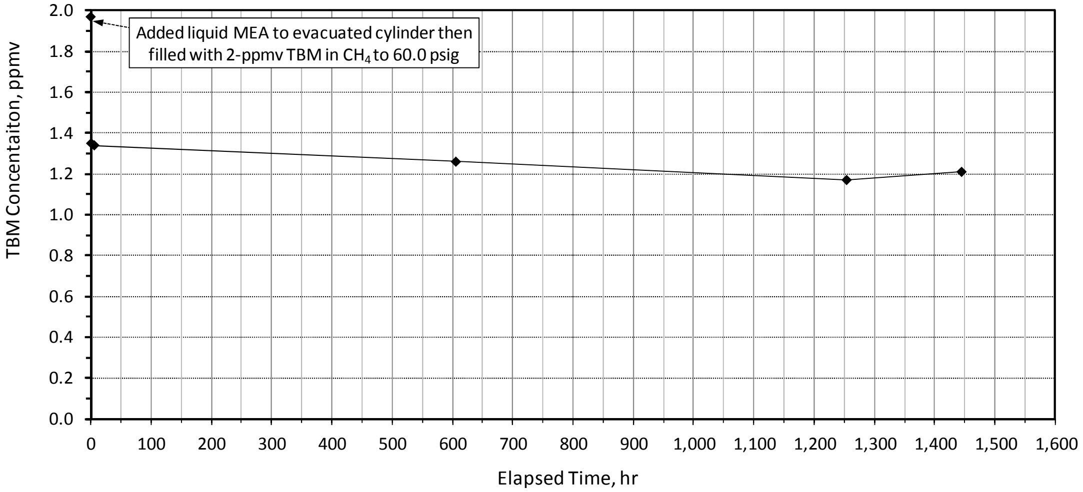


Figure 23. TBM Reactivity in the Control Reactor – Test #11 with 60 ppmv MEA Added

Statistical data ($P<0.05$ or 95% confidence limit) are presented in Table 46 and Table 47. Table 46 shows that there is no overlap in the UCL and LCL for the baseline and the experimental data. This is also demonstrated graphically in Figure 24. Table 47 shows that the null hypothesis is rejected because t experimental is greater than t critical, indicating that there is a statistical difference in the two sets of data. The conclusion is that MEA at 60 ppmv did result in odor fade.

Table 46. Statistical Data for Test #11

Statistic	Value for Test #11	Baseline Value
# of data points	5	10
t-statistic	2.78	2.26
average	1.27	1.73
standard deviation	0.08	0.11
95% Confidence Limit	0.10	0.08
Upper Confidence Limit	1.36	1.81
Lower Confidence Limit	1.17	1.66

Table 47. Comparison of Test #11 with the Baseline Test

Statistic	Pooled Value for Test #11
pooled standard deviation	0.101
t experimental	8.462
t critical	2.16
Is t experimental > t critical?	yes

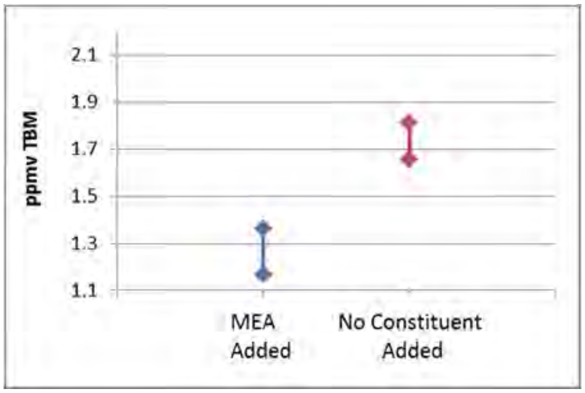


Figure 24. Graphical Demonstration of UCL and LCL for Baseline and Test #11 with 60 ppmv MEA Added

Test #12 Results (2 ppmv TBM in CH_4 with MEA in Inerted Container #4)

Test #12 used a Sulfinert-treated steel sample control reactor (Container #4) to determine the effect of a lower level of 21 ppmv MEA on TBM reactivity/loss for comparison with 60 ppmv MEA used in Test #11. In this test the cleaned and evacuated reactor was first filled to 60.0

psig with a nominal 2 ppmv TBM in CH_4 gas mixture. For an unknown reason, the TBM level declined. Therefore, several samples were taken prior to adding MEA for ~100 hours (Figure 25), so a statistical analysis could be performed. In this time period the TBM declined to 1.50 ppmv in 2.5 hours and then steadied out in the range of 1.49-1.57 ppmv.

At ~125 hours into the test the equivalent of 21 ppmv MEA was injected as a liquid into the reactor via the attached septum and the reactor was sampled over the next 1900 hours. An analysis of the reactor gas at about 70 hours after adding the TBM indicated a TBM decline to 1.22 ppmv, which steadily declined to only 1.06 ppmv in the next ~120 hours.

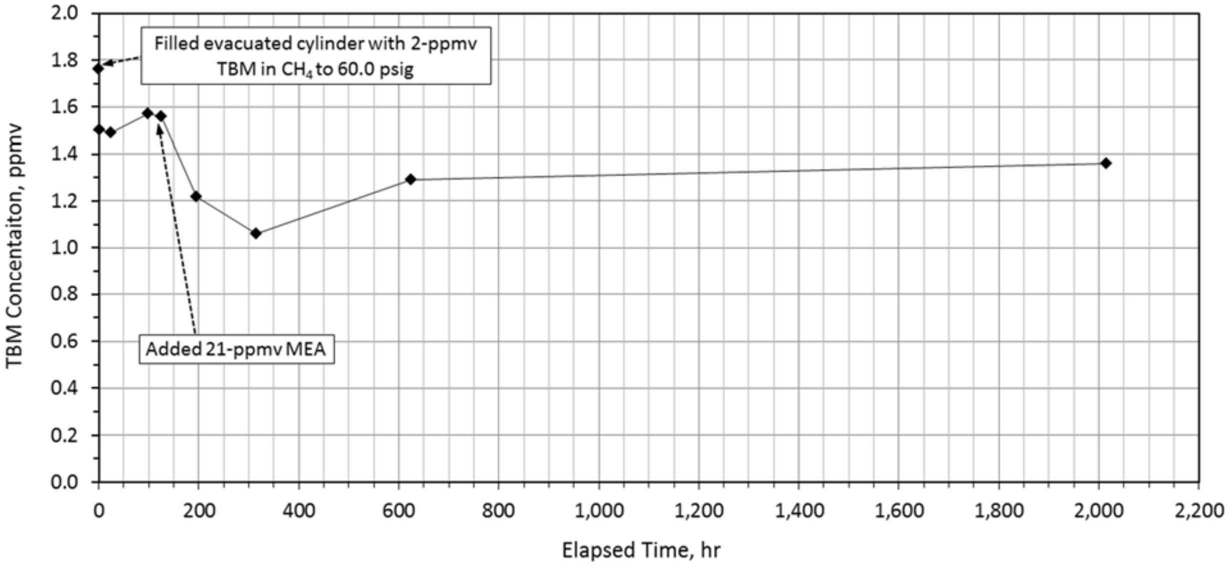


Figure 25. TBM Reactivity/Loss in the Control Reactor – Test #12 with 21 ppmv MEA Added

Statistical data ($P<0.05$ or 95% confidence limit) are presented in Table 48 and

Table 49. Table 48 shows that there is no overlap in the UCL and LCL for the baseline and the experimental data. This is also demonstrated graphically in Figure 26.

Table 49 shows that the null hypothesis is rejected because t experimental is greater than t critical, indicating that there is a statistical difference in the two sets of data. The conclusion is that MEA at 21 ppmv did result in odor fade.

Table 48. Statistical Data for Test #12

Statistic	Value for Test #12	Baseline Value
# of data points	4	4
t-statistic	3.18	3.18
average	1.23	1.53
standard deviation	0.13	0.04
95% Confidence Limit	0.20	0.06
Upper Confidence Limit	1.44	1.59
Lower Confidence Limit	1.03	1.47

Table 49. Comparison of Test #12 with the Baseline Data

Statistic	Pooled Value for Test #12
pooled standard deviation	0.095
t experimental	4.415
t critical	2.45
Is t experimental > t critical?	yes

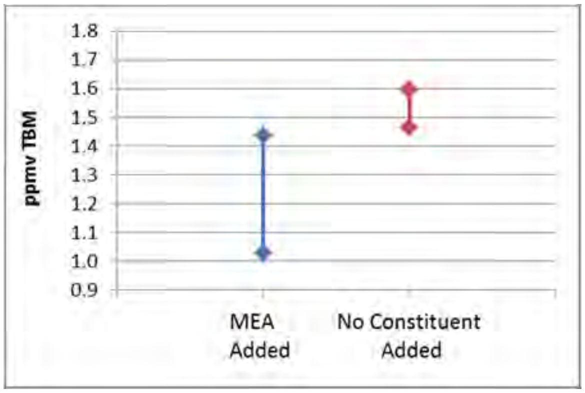


Figure 26. Graphical Demonstration of UCL and LCL for Baseline and Test #12 with 21 ppmv MEA Added

Test #13 Results (2 ppmv TBM in CH_4 with H_2O in Inerted Container #4)

Test #13 used a Sulfinert-treated steel sample control reactor (Container #5) to determine the effect of 140 ppmv H_2O (~7 lb/MMSCF) on TBM reactivity/loss. As in test #12, the cleaned and evacuated reactor was first filled to 60.0 psig with a nominal 2 ppmv TBM in CH_4 gas mixture and sampled during the next 100 hours (Figure 27) of the test prior to adding the H_2O. An analysis of the reactor gas at about 0.5 hour after adding the TBM indicated an initial TBM decline to 1.61 ppmv, which declined further to and then steadied out in the range of 1.41-1.43 ppmv over the next ~100 hours.

At 125 hours the equivalent of 140 ppmv H_2O was injected as a liquid into the reactor. An analysis of the reactor gas indicated that the TBM concentration remained essentially steady over the next 1900 hours.

Statistical data ($P<0.05$ or 95% confidence limit) are presented in Table 50 and Table 51. Table 50 shows that there is an overlap in the UCL and LCL for the baseline and the experimental data. This is also demonstrated graphically in Figure 28. Table 51 shows that the null hypothesis is not rejected because t experimental is less than t critical, indicating that there is no statistical difference in the two sets of data. The conclusion is that H_2O at 140-ppmv did not result in odor fade.

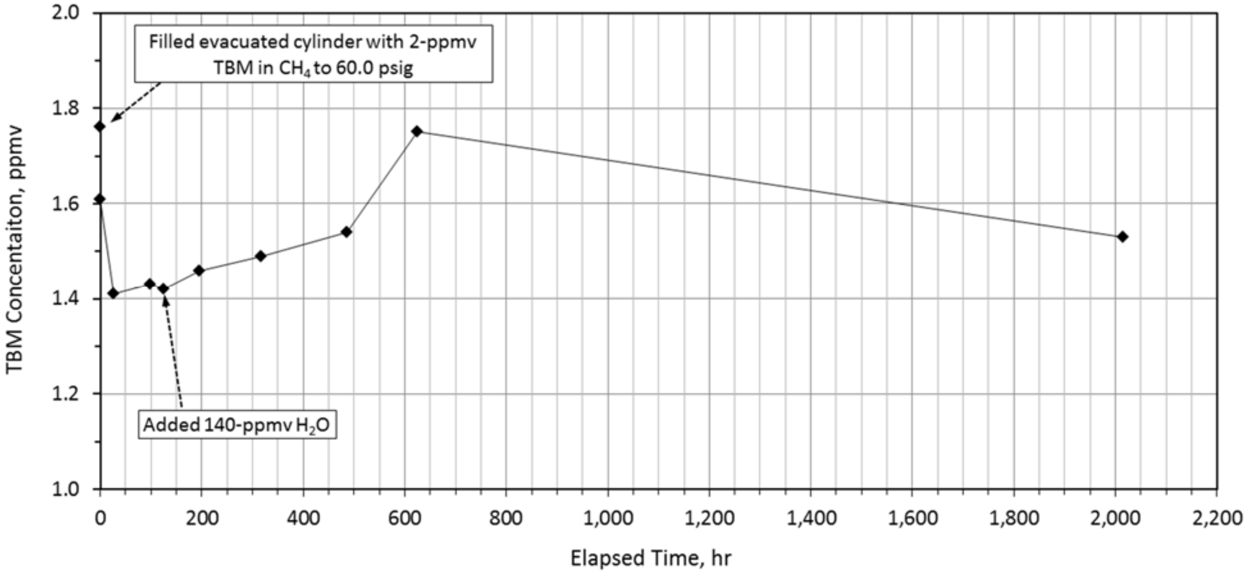


Figure 27. TBM Reactivity/Loss in the Control Reactor – Test #13 with 140 ppmv H_2O Added

Table 50. Statistical Data for Test #13

Statistic	Value for Test #13	Baseline Value
# of data points	6	3
t-statistic	2.57	4.30
average	1.55	1.48
standard deviation	0.12	0.11
95% Confidence Limit	0.12	0.27
Upper Confidence Limit	1.65	1.76
Lower Confidence Limit	1.41	1.21

Table 51. Comparison of Test #13 with the Baseline Data

Statistic	Pooled Value for Test #13
pooled standard deviation	0.114
t experimental	0.598
t critical	2.36
Is t experimental > t critical?	no

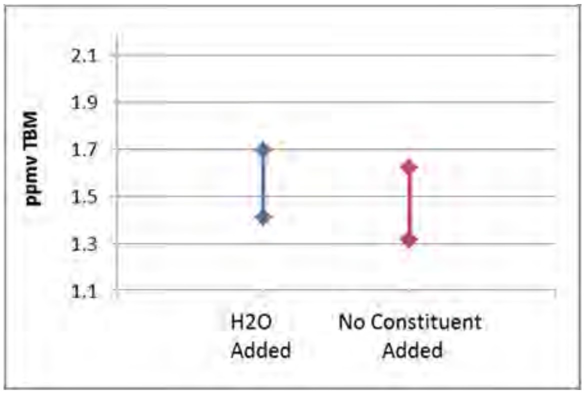


Figure 28. Graphical Demonstration of UCL and LCL for Baseline and Test #13 with 140 ppmv H_2O Added

Test #14 Results (2 ppmv TBM in CH_4 in Off-the-Shelf Steel Pipe Containers #2B and #2C at Different Temperatures)

Test #14 used an unused off-the-shelf steel pipe (Container #2B and #2C) to determine the temperature effect of the iron oxide surface on TBM reactivity/loss. Two evacuated reactors were filled to 60.0 psig with the nominal 2 ppmv TBM in CH_4 gas mixture and sampled during the next 500 to 1200 hours (Figure 29).

The reactor at 70°F slowly declined over time to near the detection limit, while the reactor at 34°F held steady around 1.5 ppmv after an initial small decline. This is consistent with the expectation that the reaction of TBM with iron oxide surface would be promoted by temperature. This data was used to estimate the Arrhenius reaction rate used in the first Ansys modeling.

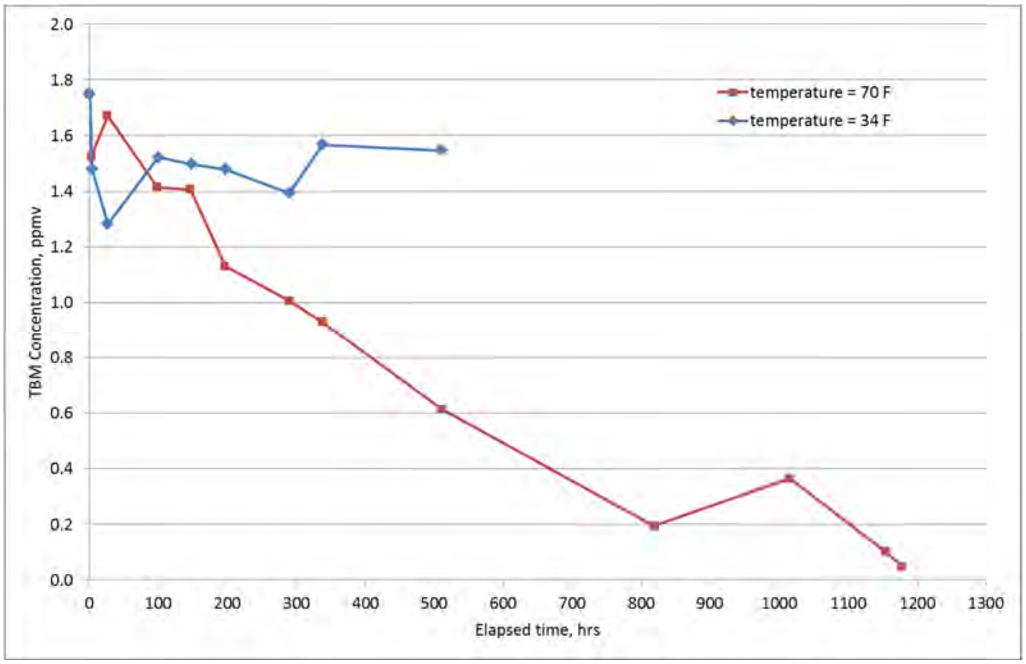


Figure 29. TBM Reactivity/Loss in Reactors #2B and #2C – Test #14 at Two Different Temperatures

Test #15 Results (4 ppmv THT in Synthetic Natural Gas in Plastic Container #3B and #3C at Different Temperatures)

Test #15 used specimens of the plastic pipe (Container #3B and #3C) to determine the temperature effect of THT absorption. Two evacuated reactors were filled to 60.0 psig with the nominal 4 ppmv THT in a synthetic natural gas mixture and sampled during the next 500 hours (Figure 30). The reactor at 70°F had an initial sharp decline followed by a slower decline to around 1 ppmv. The reactor at 34°F also had a sharp decline but to a lower concentration. It appears to be steady at around 0.3 ppmv. Since the phenomenon for plastic pipe is a surface absorption/adsorption versus a reaction, there may be some loss at the lower temperature. While adsorption is an exothermic process, entropy of the system is also decreased due to a decrease in the freedom of movement of the molecules. Adsorption is thermodynamically more favorable at lower temperatures.

This data was used to estimate the Arrhenius reaction rate used in the first Ansys modeling.

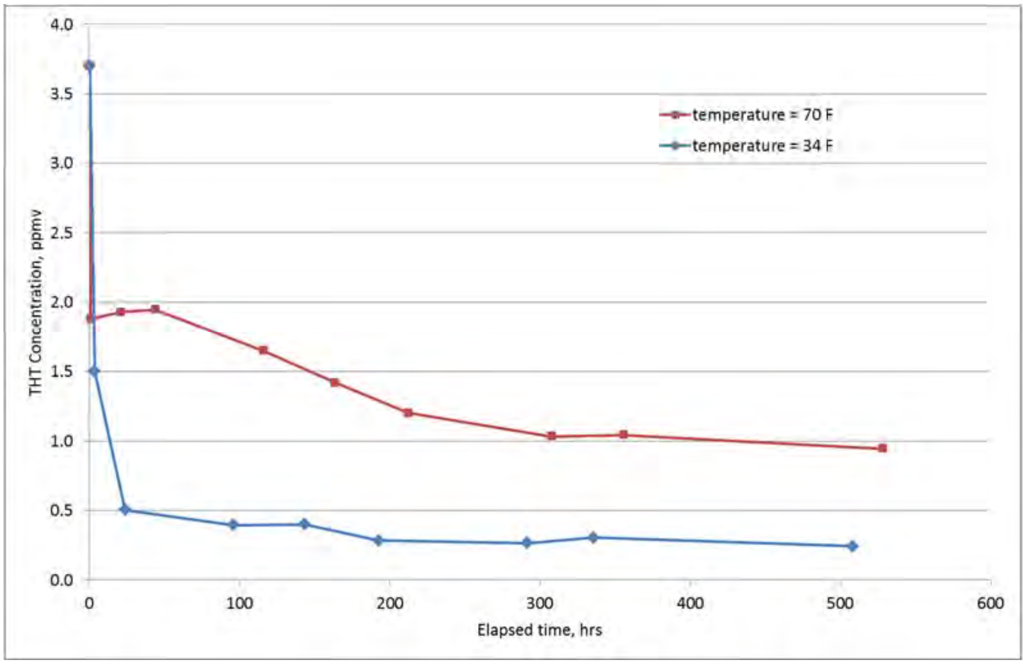


Figure 30. THT Reactivity/Loss in Reactors #3B and #3C – Test #15 at Two Different Temperatures

Test #16 Results (4 ppmv THT in Synthetic Natural Gas in Off-the-Shelf Steel Pipe Containers #2D and #2E at Different Temperatures)

Test #16 used an unused off-the-shelf steel pipe (Container #2D and #2E) to determine the temperature effect of the steel surface on THT reactivity/loss. Two evacuated reactors were filled to 60.0 psig with the nominal 4-ppmv THT in a synthetic natural gas mixture and sampled during the next 360 hours (Figure 31). Both reactors experienced an initial decline but reached equilibrium quickly. The reactor at 70°F equilibrated to 1.6-ppmv, while the reactor at 34°F equilibrated at 1.2 ppmv. This temperature effect is opposite to what is observed with the TBM in steel experiment at different temperatures, and is consistent with the expectation that the reaction of THT is more of a surface phenomenon rather than reactivity with the iron oxide.

This data was used to estimate the Arrhenius reaction rate used in the first Ansys modeling.

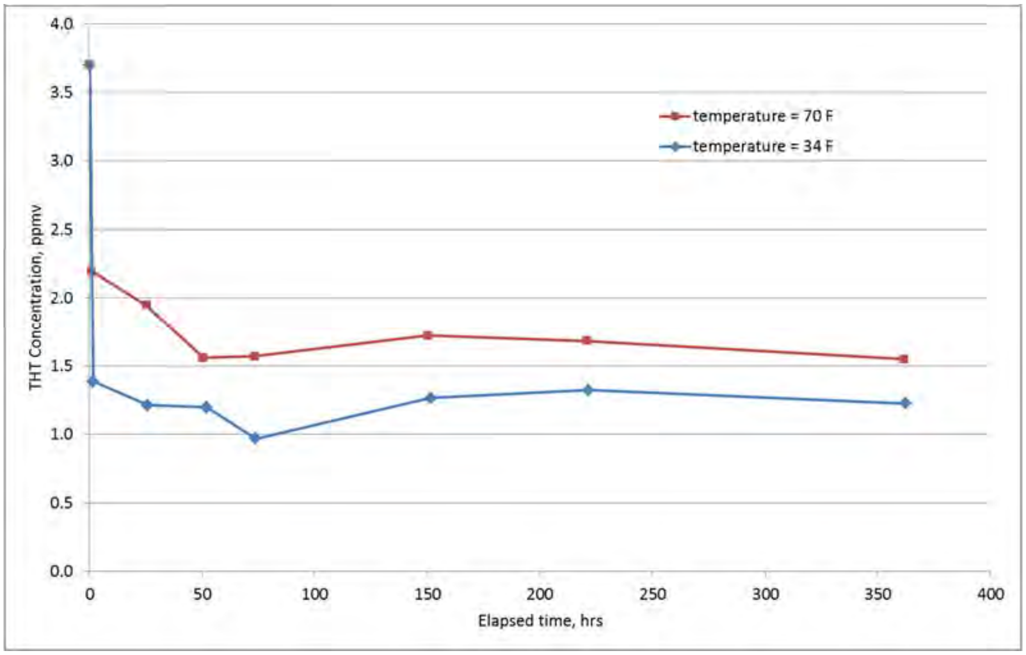


Figure 31. THT Reactivity/Loss in Reactors #2D and #2E – Test #16 at Two Different Temperatures

Test #17 Results (2 ppmv TBM in CH_4 in Plastic Containers #3D and #3E at Different Temperatures)

Test #17 used specimens of the plastic pipe (Container #3D and #3E) to determine the temperature effect of TBM absorption/adsorption. Two evacuated reactors were filled to 60.0 psig with the nominal 2-ppmv TBM in CH4 gas mixture and sampled during the next 1000 hours (Figure 32). The reactor at 70°F slowly declined over time to near 0.2-ppmv, while the reactor at 34°F held steady around 1.0 ppmv after an initial small decline. This is opposite to what was observed with the THT in plastic experiment (Test #15) and consistent with absorption of the TBM at different temperatures.

This data was used to estimate the Arrhenius reaction rate used in the first Ansys modeling.

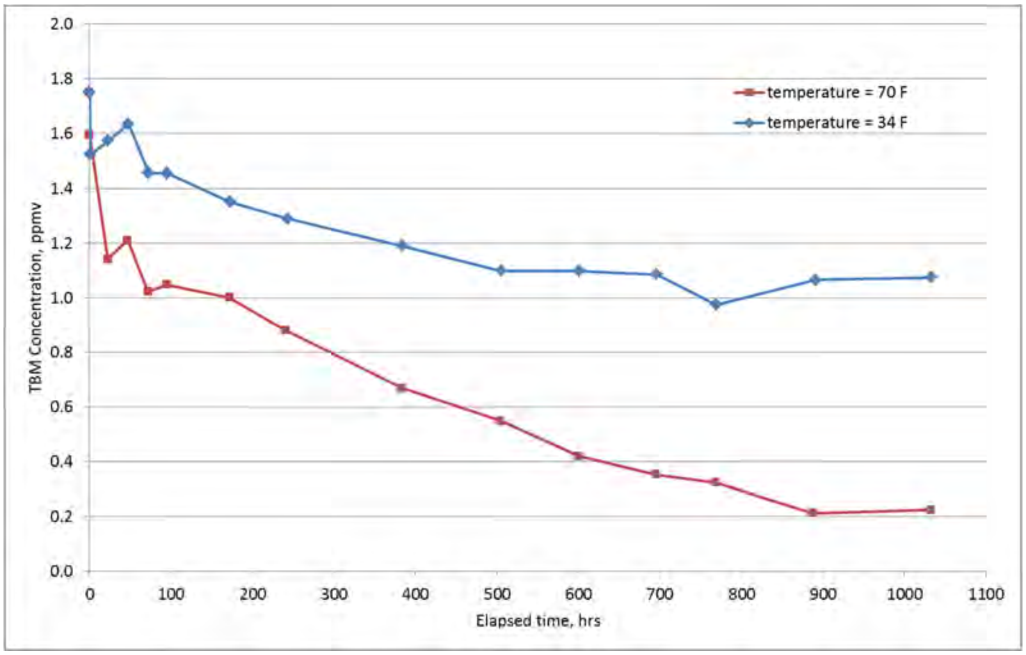


Figure 32. TBM Reactivity/Loss in Reactors #3D and #3E – Test #17 at Two Different Temperatures

Test #18 Results (2 ppmv TBM in CH_4 with 2-ppmv MM in Inerted Container #5

Test #18 used a Sulfinert-treated steel sample control reactor (Container #5) to determine the effect of methyl mercaptan (MM), a naturally occurring sulfur compound, on TBM reactivity/loss. The cleaned and evacuated reactor was first filled to 30 psig with a nominal 2-ppmv TBM in CH4 gas mixture and sampled during the next 100 hours of the test prior to adding the MM. The final pressure volume was 60 psig. An analysis of the reactor gas at about 24 hours later indicated slight TBM and MM declines which steadied out over the next ~200 hours (Figure 33).

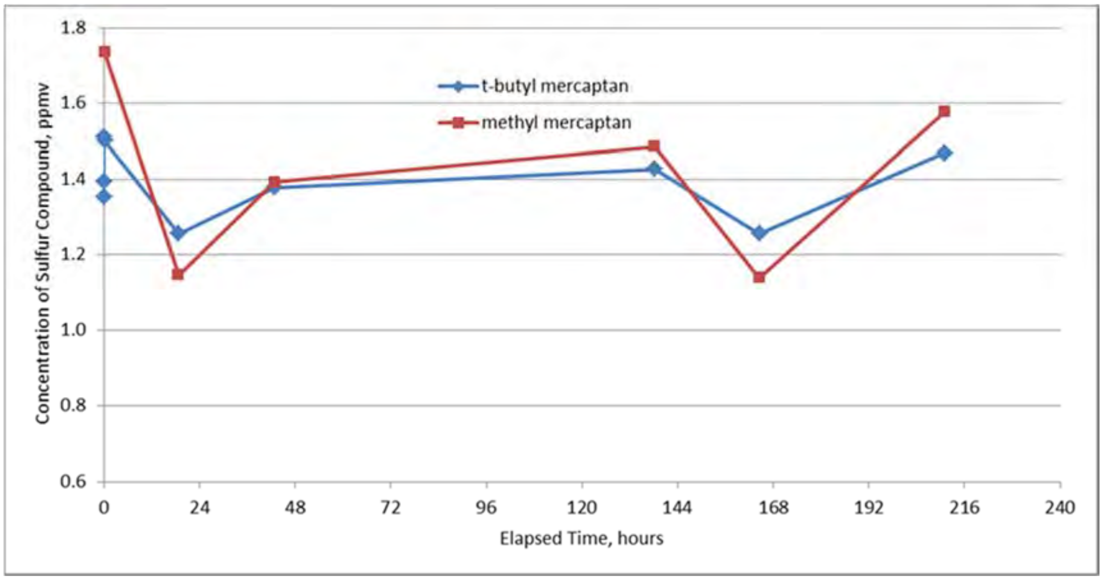


Figure 33. TBM Reactivity/Loss in the Control Reactor – Test #18 with Methyl Mercaptan Added

Statistical data ($P<0.05$ or 95% confidence limit) are presented in Table 52 and Table 53. Table 52 shows that there is an overlap in the UCL and LCL for the baseline and the experimental data. This is also demonstrated graphically in Figure 34. Table 53 shows that the null hypothesis is not rejected because t experimental is less than t critical, indicating that there is no statistical difference in the two sets of data. The conclusion is that in this experiment methyl mercaptan did not result in odor fade. This contradicts earlier information[32-34] obtained in the literature search and is a topic for further investigation.

Table 52. Statistical Data for Test #18

Statistic	Value for Test #18	Baseline Value
# of data points	6	3
t-statistic	2.57	4.30
average	1.38	1.42
standard deviation	0.11	0.08
95% Confidence Limit	0.11	0.20
Upper Confidence Limit	1.49	1.62
Lower Confidence Limit	1.27	1.22

Table 53. Comparison of Test #18 with the Baseline Data

Statistic	Pooled Value for Test #18
pooled standard deviation	0.099
t experimental	0.547
t critical	2.36
Is t experimental > t critical?	no

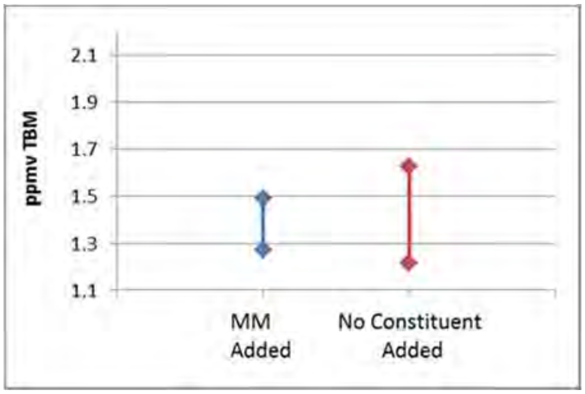


Figure 34. Graphical Demonstration of UCL and LCL for Baseline and Test #18 with Methyl Mercaptan Added

Test #19 and #20 Results (2 ppmv TBM in CH_4 with 4-ppmv THT in Plastic and Steel Containers 2F, 2G, 3F, and 3G

This set of tests was designed to yield new reaction rates for the competition of TBM and THT to the active sites since previous data sets were showing an over consumption of odorant (further discussed in the modeling section). Unfortunately, the equipment to dose the reactors had been disassembled several months earlier. The parts were reassembled but the resulting data set was poor. In all cases, the data led to negative Activation Energies. The prior four datasets for TBM and THT in plastic and steel individually all had positive Activation Energies. This data was abandoned in favor of data collected from four different temperatures.

Test #21 Results (2 ppmv TBM in CH_4 in Plastic Containers 3H, 3I, 3J, and 3K at Different Temperatures)

Test #21 used specimens of the plastic pipe to determine the temperature effect of TBM absorption/adsorption. Four evacuated reactors were filled to 60.0 psig with the nominal 2-ppmv TBM in CH4 gas mixture and placed in separate temperature controlled areas (coolers, rooms, and ovens). Each reactor was sampled over the next few days (Figure 35). The following observations were made:

- The warmest reactor at 140°F (purple) rapidly declined over 500 hours to a non-detectable amount.
- The reactor at 104°F (green) also declined rapidly and began to level out around 0.3 ppmv.
- The 72°F room temperature reactor (red) had a slower loss of odorant to around 0.9 ppmv.
- The 40°F coldest reactor (blue) had the least amount of odorant loss.
- As expected, TBM loss was higher in the hotter specimens.
- The rate of loss was also higher in the hotter specimens.

This data was consistent with absorption of the TBM at different temperatures. It was the phenomena and trend that was expected. This data was used to estimate the Arrhenius reaction rate to be used in the second Ansys modeling effort.

Test #22 Results (4 ppmv THT in Synthetic Natural Gas in Plastic Containers 3L, 3M, 3N, and 3O at Different Temperatures)

Test #22 used specimens of the plastic pipe to determine the temperature effect of THT absorption/adsorption. Four evacuated reactors were filled to 60.0 psig with the nominal 4-ppmv THT in a synthetic natural gas mixture and placed in separate temperature controlled areas (coolers, rooms, and ovens). Each reactor was sampled over the next few days (Figure 36). The following observations were made:

- THT loss was higher in the hotter specimens.
- The rate of loss was slightly higher in the hotter specimens.
- This is a different trend than what was seen in the first round of testing.
- There is a slight anomaly with the final room temperature data. Could this be an equilibrium reaction?

Overall this data was consistent with absorption of the TBM at different temperatures, and was the phenomena and trend that was expected. This data was used to estimate the Arrhenius reaction rate to be used in the second Ansys modeling effort.

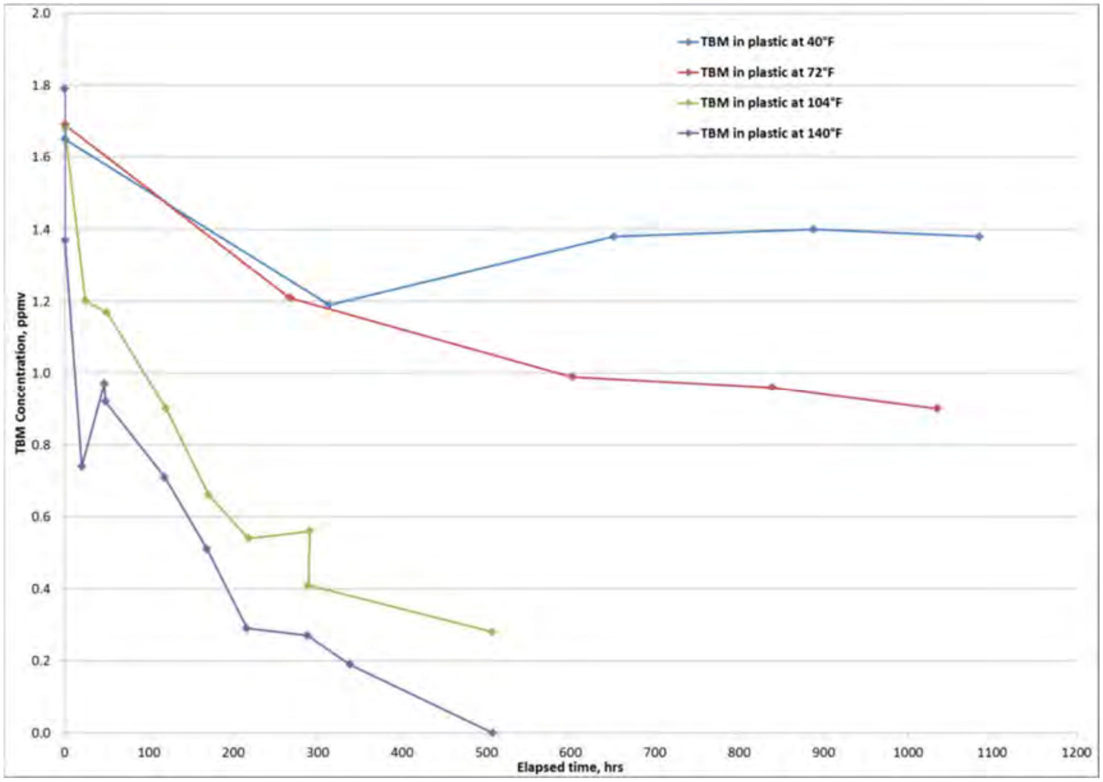


Figure 35. TBM Reactivity/Loss in Plastic Pipe – Test #21 at Four Different Temperatures

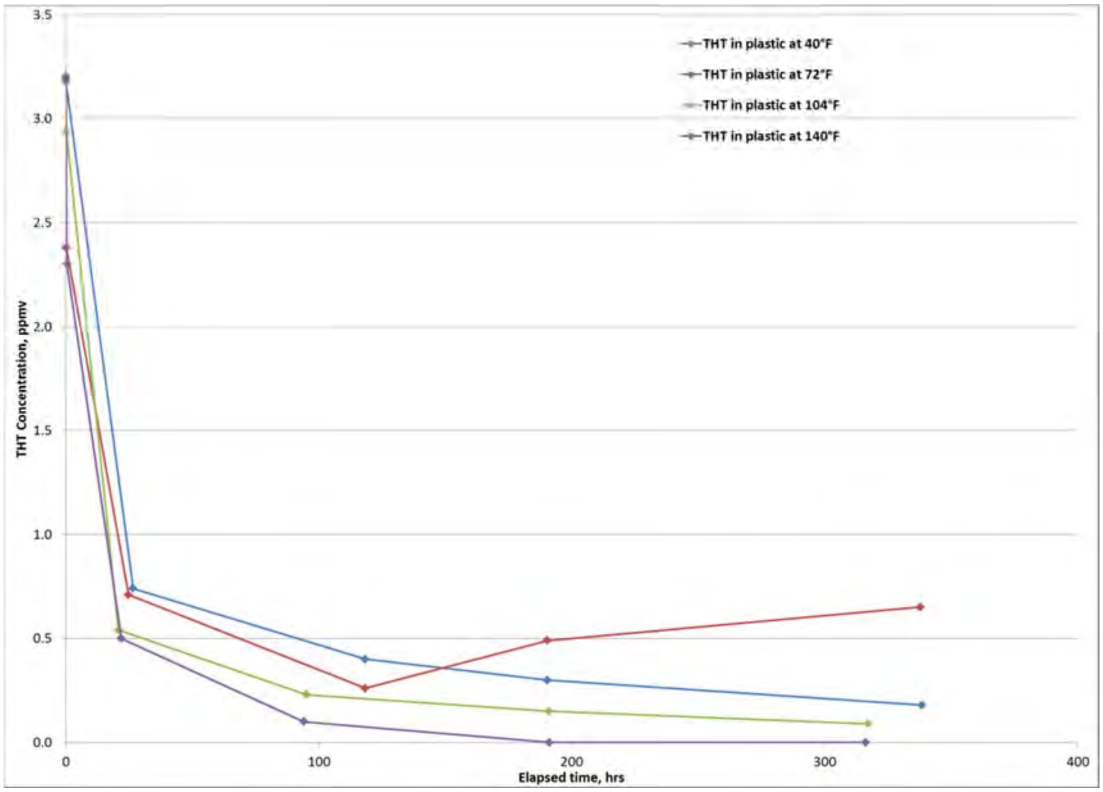


Figure 36. THT Reactivity/Loss in Plastic Pipe – Test #22 at Four Different Temperatures

Test #23 Results (2 ppmv TBM in CH4 in Steel Containers 2H, 2I, 2J, and 2K at Four Different Temperatures with H_2O at 1300 ppmv)

Test #23 was designed to estimate the Arrhenius reaction rate of TBM in a steel pipe with the addition of water. The rationale for this is because water has an impact on the reaction rate of TBM due to its presence as a reaction byproduct and its probable inclusion in the rust molecular formula. Most rust compounds are not anhydrous (dry) but instead have water molecules loosely associated as water of hydration. The derivations are described in further detail in the New Ansys Modeling section.

Four evacuated reactors were filled to 60.0 psig with the nominal 2-ppmv TBM in CH4 gas mixture and placed in separate temperature controlled areas (coolers, rooms, and ovens). Each reactor was sampled over the next few hours. The reactions occurred very quickly as seen in Figure 37. The following observations were made:

- The TBM faded very quickly at all temperatures.
- The cold reactor exhibited the least amount of fade, as would be expected as temperature would inhibit the reaction. All other temperatures faded to BDL.
- Di-t-butyldisulfide was found in the hottest reactor only.
- The 104°F data is slightly anomalous, but the data point still fits on the reaction rate curve.

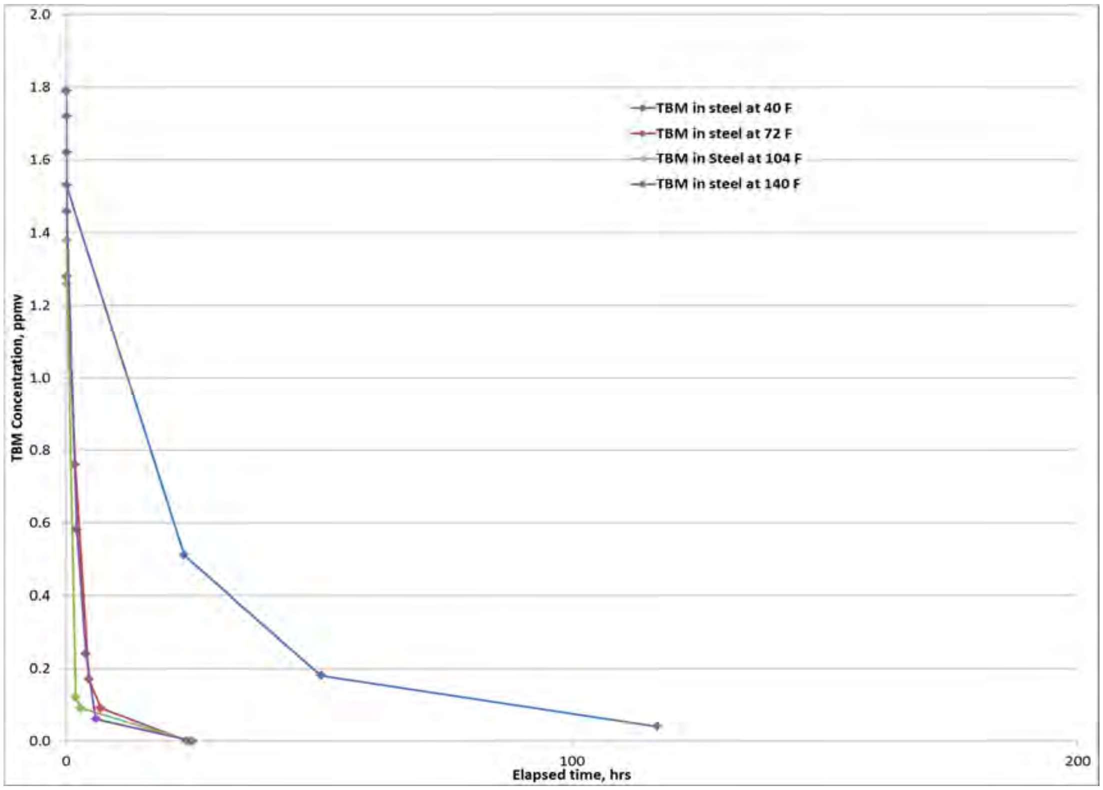


Figure 37. TBM Reactivity/Loss in Steel Pipe – Test #23 at Four Different Temperatures

Developing a Simplified Odor Fade Model – Initial Model Development

This goal was hampered by the little available data from the literature. The surveys were designed to help remediate the lack of data, but response was limited. In order to help meet this goal, three approaches were ultimately taken, 1) to look at a past project performed in the mid-sixties, 2) to take an empirical approach with the data that does exist, and 3) use Ansys Fluent modeling based on lab experiments.

AGA Project PB-48

Past research gives some good insights on developing equations to model odor fade in steel pipe. In the early to mid-sixties the Institute of Gas Technology (IGT, the predecessor to the current GTI) worked on a project funded by the American Gas Association (AGA).[32,33,34] This project was designed to study the stability of mercaptans under pipeline conditions by flowing alkyl mercaptan containing gas through a bench scale reactor packed with rusted steel spheres.

The principle investigator of the project, James L. Johnson, based the initial equations on earlier work in coal gasification systems by C.G. Von Fredersdorff. The IGT/AGA project found that the mercaptan conversion rate obeyed a first-order rate law based on the concentration of reactive sites on and within an oxide surface. The process appeared to take place in three distinct steps. Johnson states in his 1967 report to AGA that "There is an initial period of complete conversion of mercaptan to disulfide, a period of rapidly decelerating conversion, and a final low-rate period where conversion rates asymptotically approach zero. This type of behavior was exhibited in practically all tests conducted in this study, although, in some cases, the initial period of complete conversion was absent." Figure 2 from the Johnson paper, a typical conversion rate vs. time curve, is reproduced in Figure 38 below.

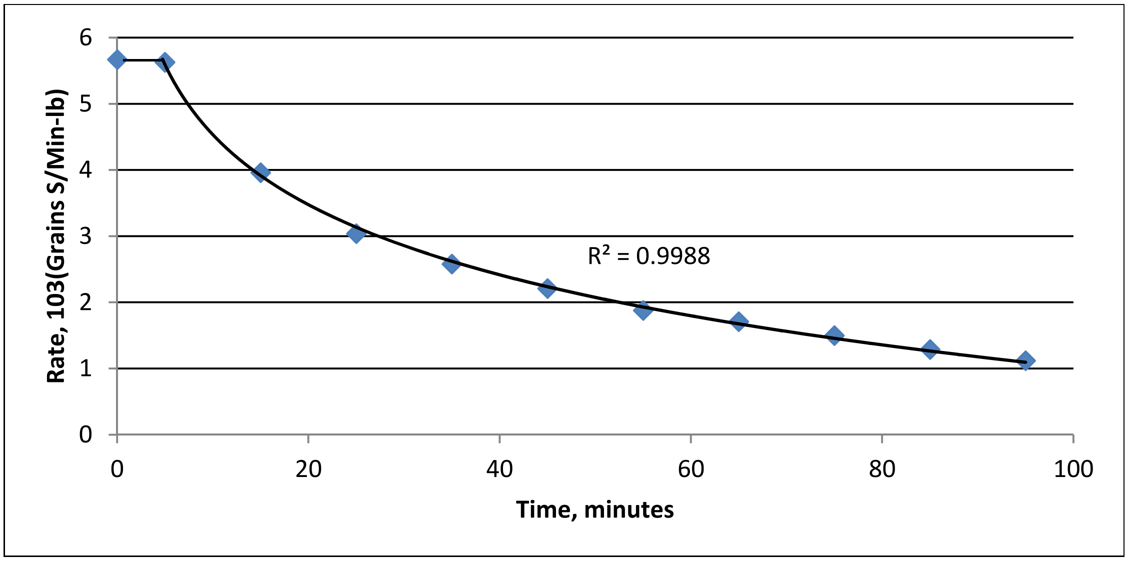


Figure 38. Typical Mercaptan Conversion Rate, from Johnson AGA Reference (Figure 2)

This behavior was seen in most of the tests performed. The authors surmised that the most reasonable explanation for the leveling off and subsequent slower reaction rate of mercaptan was that two different rate laws were in play. The initial reaction where the odor faded immediately is a heterogeneous reaction in which the reactant (iron oxide) is rapidly deactivated:

gas phase reactant + solid reactant → reaction product + deactivated solid reactant

In his tests, Johnson found that the deactivated iron oxide could be regenerated by exposure to oxygen. However, little oxygen is found in typical natural gas streams. GTI's current experiments show that there is no effect from oxygen in the TBM concentration in the inerted test containers, i.e. if no iron oxide is present. The deactivation appears to rely solely on the inherent oxygen present in the iron oxide rust.

The second reaction phase is a period of rapidly decelerating loss of odorant. The project found that a correlation between the time elapsed and the mercaptan concentration at the outlet of the experiment. Adapted to a pipeline configuration (and minus the oxygen dependence factor) the equation is:

$$\sqrt{Y_o} - \sqrt{Y} = \frac{k_o f P(\frac{\pi D L}{G})}{(t+b)^{2/3}}$$

Where

Y_o = the initial concentration
Y = the final concentration
K_o = kinetic rate constant
f = kinetic parameter dependent on mercaptan type
P = pressure
D = inner diameter
L = length of pipe from where mercaptan is introduced to where it is measured
G = gas flow rate
t = the time of exposure
b = kinetic parameter dependent on temperature and rustiness of surface

The equation can be rearranged into a form equivalent to a linear response where x is time and y is a combination of the kinetic parameters, mercaptan concentrations, pressure, diameter, length, and gas flow. A plot of the Y combination versus time should yield a straight line, the slope of which is related to the Y parameters and the x-intercept related to b.

$$y = mx + b$$

The goal was to minimize the difference (amount of odorant loss) between the initial mercaptan concentration and the final concentration.

Empirical Approach

The empirical approach looks at the observations compiled from the literature and the surveys. The amount of odorant added is calculated as ml per square foot of the pipe internal surface area in some cases, and as ml per length of pipe in others, depending on the x parameter. The following general observations can be made.

Temperature: Raising the gas temperature can have opposing effects. In the adsorption process, a higher temperature will drive off the adsorbed molecule. The rate of adsorption of a gaseous molecule on a surface is inversely proportional to gas temperature. But, any odorant molecule in contact with the surface will have a greater chance of undergoing oxidation from surface rust due to the temperature effect on the rate of oxidation (the reaction rate increases at higher temperatures).

Initial loss of mercaptan seems to be greater at lower temperatures. Lowering the temperature increases the probability of both absorption and adsorption, and gives oxidation from surface rust a greater chance to occur due to increased residence time despite the reduced rate of oxidation.

The temperature data available from the literature and the surveys seem to be similar in magnitude. The laboratory data seems to contradict this somewhat as described in the previous section.

Pressure: An increase in gas pressure will induce increased absorption and adsorption, and concurrently an increase in oxidation from surface rust and odor fade. Changing the gas line pressure can also impact the flow rate if all other conditions remain similar. Laminar flows will decrease with reduced pressure; turbulent flows (possibly due to oversized pipe) may increase with lower pressure, if the flow transitions from a turbulent to a laminar regime.

The available literature and survey data seem to show some correlation with pressure. Figure 39 is a plot of odorant added to eliminate odor fade versus pipeline pressure. Higher pressures required more odorant to be added. The correlation appears to be linear ($R^2 = 0.91$).

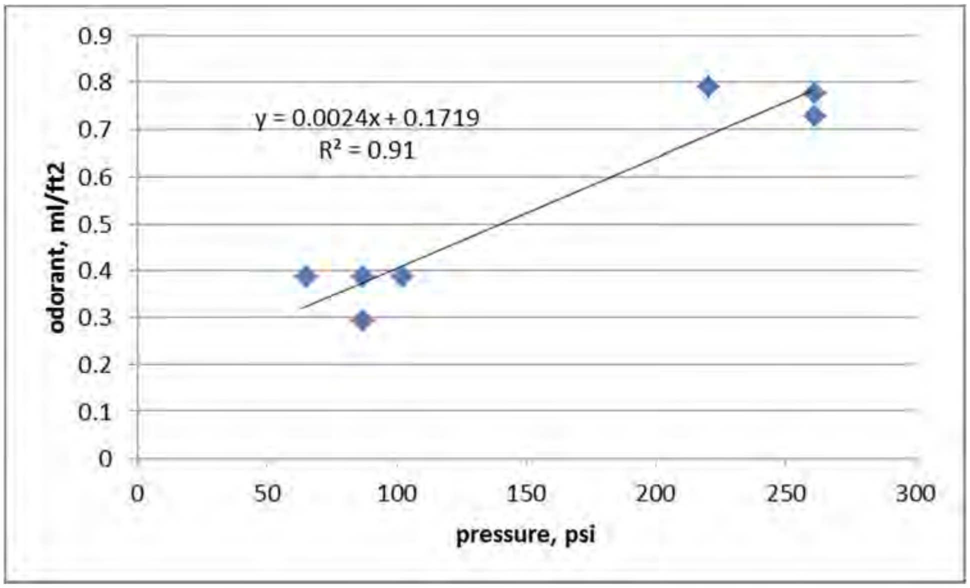


Figure 39. Odorant Addition Correlation with Pressure

Flow Rate: Odorant fade can occur under low flow conditions because diffusion of the odorant molecules is more probable with the increased residence time. Increasing the gas flow rate decreases the residence time and the likelihood of odor fade lessens. One study recommended maintaining a minimum gas velocity of 10 ft/sec (0.036 MMSCF) in the pipeline to prevent odor fading due to stagnation.

As gas flows through a pipe, the flow can be characterized by two different mechanisms, generally depending on the flow rate. Laminar flow occurs with low velocities, the gas flows in parallel layers, with no disruption or mixing between the layers. Turbulent flow is the opposite. It occurs at higher velocities with significant mixing and eddy currents.

The available literature and survey data seem to show little correlation with flow. Figure 40 is a plot of odorant added to eliminate odor fade versus flow in MMSCFH. The odorant is plotted by both ml per square feet surface area and by ml per length. Considerable scatter in the data is seen. Flow will not be investigated in further detail.

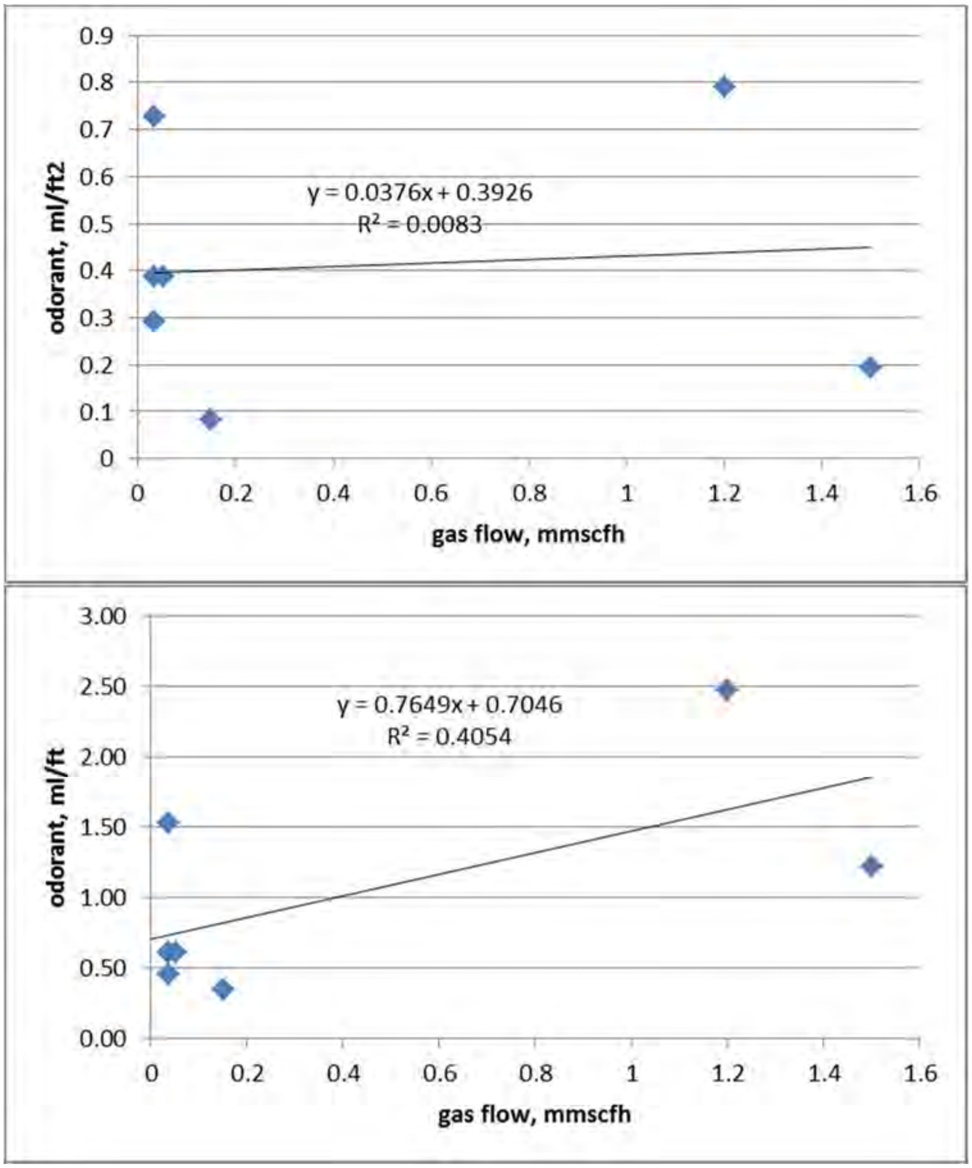


Figure 40. Odorant Addition Correlation with Gas Flow

Surface Area and Pipe Diameter: As the pipeline moves toward the end user, the diameter of the pipe tends to decrease. This lowers the gas volume- to- interior- surface- area ratio and increases the potential surface interaction. The more surface area available, the more physical processes such as adsorption and absorption will occur. This is true for both the bare metal and any entrained iron oxide coating. Physically, the powdery surface area of the iron oxides is greater than the bare metal. The greater the surface area the greater is the affinity to adsorb odorant.

The available literature and survey data seem to show some correlation with pipe diameter. The following graph is a plot of odorant added to eliminate odor fade (in ml per length) versus diameter in inches. Larger pipes required more odorant to be added. The correlation could be linear but it is hard to judge without more data.

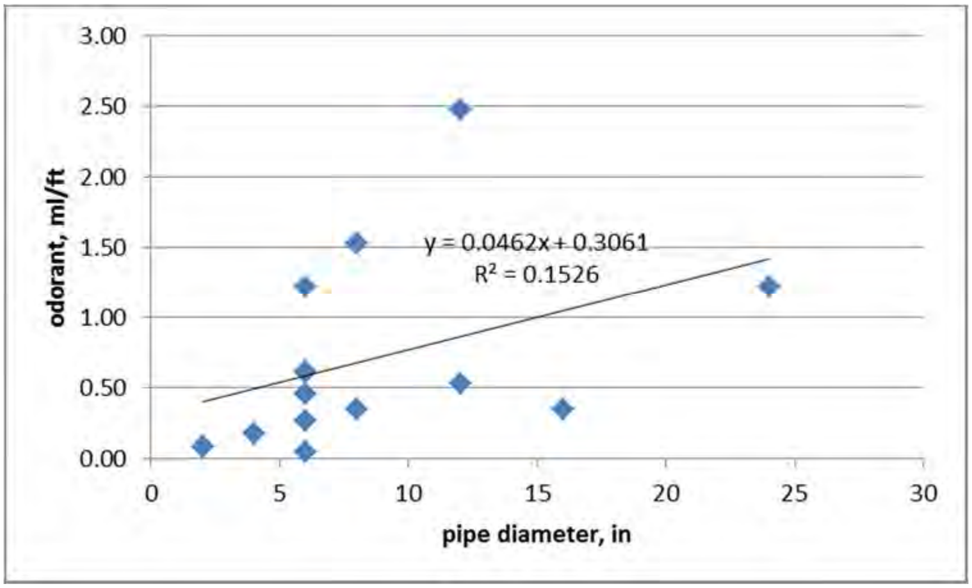


Figure 41. Odorant Addition Correlation with Pipe Diameter

Developing a Simplified Odor Fade Model - Ansys Fluent Modeling

In order to better understand the decomposition of odorant in the gas phase, a computational fluid dynamic model was generated based on literature data and laboratory data using ANSYS Fluent. This software contains the broad physical modeling capabilities needed to model flow, turbulence, heat transfer, and reactions for a variety of industrial applications. The loss of natural gas odorants was modeled using various methods of gas-phase chemistry.

Model Setup

The pipe was modeled as a 2D-axisymmetric plane, representing the full 3D pipe (Figure 42). This requires the assumption that all circumferential gradients be zero, which is expected for this typical pipe geometry. The first set of simulations was performed in a steady state mode. The remaining simulations using GTI data were done with time dependent (transient) modeling. The computational grids are coarse near the centerline (axis) and fine near the surface, where reactions take place. In terms of models employed, the following parameters were used in addition to those required by the flow field (mass, momentum, and energy conservation).

Turbulence: k-ω with shear stress transport modeling, demonstrated accuracy for 2D axisymmetric modeling.

Radiation: Radiation is assumed to be negligible.

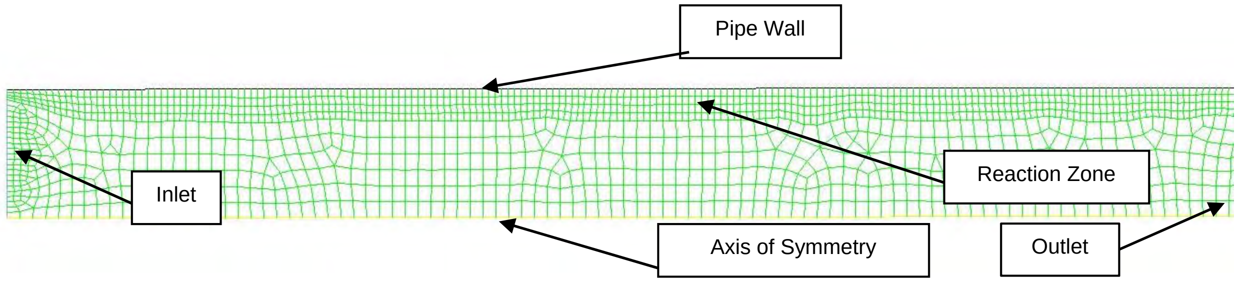


Figure 42. Example Diagram of 2D Pipe Segment

Species Transport and Reaction

In all cases the chemistry is modeled as a surface reaction; with a volumetric chemistry modeled for the row of cells adjacent to the wall. Two types of pipe are modeled, steel and plastic, specifically MDPE, and for the former both bare and rusted pipe were simulated. The 'rust' is not directly modeled, but rather its presence and influence on reaction rate kinetics was embedded in the reaction parameters.

In general, the odorant loss was modeled as a 1-step global mechanism, a decomposition of tert-butyl mercaptan (TBM) in the presence of rust, the adsorption of TBM to plastic pipe (MDPE), and an adsorption of tetra-hydrothiopene (THT) to steel or plastic pipe (MDPE). The reaction of TBM with rust takes place across the inner pipe wall. The mechanisms are 1-step global mechanisms as follows:

- decomposition of TBM (Equation 1)
- adsorption/absorption of tetrahydrothiophene (THT) to steel, and medium density polyethylene pipe (MDPE) (Equation 2)

Equation 1: $2\ (CH_3)_3CSH \rightarrow (CH_3)_3CS\text{-}SC(CH_3)_3 + H_2$

Equation 2: $(CH_2)_4S(g) \rightarrow (CH_2)_4S(s)$

The first modeling effort used information derived from data found in paper reported at the 1992 Odorization Symposium, for a rusted 12 ft. pipe with a ¼″ I.D. (Moran, 1992).[54] The remaining modeling efforts used GTI laboratory data as presented perviously.

Materials

In the gas phase, the 'bulk' natural gas is modeled as methane, with trace amounts of odorants, and gaseous hydrogen as a surrogate by-product in the decomposition reaction. The odorants will have the properties defined as follows (in SI units per simulation requirements):

Table 54. Thermophysical Properties of the Odorant Reactants

	TBM	Di-t-butyl Disulfide	THT
Molecular Weight (kg/kgmol)	90.19	178.38	88.19
Density (kg/m^3)	*Initially approximated as an Ideal Gas*		
Specific Heat (J/kg·K)	2.4*T + 416.3	3.1*T + 283.4	3.1*T + 283.4
Thermal Conductivity (W/m·K)	1.24e-2	1.49e-2	1.45e-2
Dynamic Viscosity (kg/m·s)	7.38e-4	4.26e-4	4.26e-4
Standard State Enthalpy (J/kgmol)	-1.087e+8	-1.998e+8	-1.998e+8
Standard State Entropy (J/kgmol·K)	1.127e+6	1.519e+6	1.519e+6

Derivation of Arrhenius Parameters

At the surface, the turbulent-chemistry reaction was assumed to be laminar finite-rate, meaning that the reactions are assumed not to be limited primarily by turbulent mixing. This is appropriate for simulations largely recreating "lock up" or no flow conditions. For the surface reaction, the formula in Equation 3 applies for the volumetric reaction rate. Following Arrhenius kinetics, the pre-exponential constant (A) and activation energy (E_A) must be provided. These are derived as follows.

Equation 3:

$$\dot{\omega} = A \cdot exp^{-E_A/RT}$$

Where the units are expressed as

$$[\omega] = [A] = \text{kgmol/m}^3\text{·s} \qquad [E_A] = \text{J/kgmol}$$

Taking the logarithm of both sides of Equation 3 yields:

Equation 4:

$$\ln(\dot{\omega}) = \ln(A \cdot exp^{-E_A/RT})$$

which rearranges to:

$$\ln(\dot{\omega}) = \ln(A) + \ln(exp^{-E_A/RT})$$

and finally rearranges to:

Equation 5: $$\ln(\dot{\omega}) = \ln(A) - \frac{E_A}{R}\left(\frac{1}{T}\right)$$

Charting this relationship using the linear equation y = mx +b, where

$$y = \ln(\dot{\omega})$$

$$m = -\frac{E_A}{R}$$

$$x = \left(\frac{1}{T}\right)$$

$$b = \ln(A)$$

The process of deriving Arrhenius rate parameters from experimental data for the 1-step reduced mechanism is straightforward. The loss of a given odorant is tracked over time in static conditions (temperature, pressure, etc.). With odorant loss vs. time known for at least two temperature points, the data is graphed as concentration (y) vs time (x). The slope and intercept information determined from the linear fit will allow the calculation of the required parameters.

Using the intercept data "b", we rearrange to get the following:

$A = \exp^b$ where A is expressed in kgmol/s (same units as ω).

To convert to the proper units the volume used to derive the data is required (in units of m^3), and is divided into the result to get kgmol/m^3s.

In the same manner, using the slope of the line "m", we get

$$m = -\frac{E_A}{R}$$

$$E_A = -(m * R)$$

Substituting the gas constant R = 8.314 J/kgmolK, yields E_A in J/kgmol.

In each of the succeeding model efforts, this format for deriving the needed parameters was followed, with some modifications as necessary based on the precise model parameters used.

First Modeling Effort – Literature Data

The first draft model uses a parametric analysis to determine the loss of odorant, with a combination of tertiary-butyl mercaptan (TBM) and its dimer decomposition product, di-t-butyl disulfide. The model was performed for a 100 ft. long section of 2″ and 4″ pipes, which is sufficiently long to reach fully developed flow. Flow rates used in the simulations were 2.94 cubic feet per minute (CFM), 210 CFM, as well as lock-up (i.e. no flow) condition.

The pre-exponential constant (A) and activation energy (E_A) were derived from the TBM loss data shown in Table 55 and resulted in the following graph (Figure 43).

Table 55. TBM Loss Data

State Point	Steady State Consumption TBM Rate (kgmol/s)	Temperature (°K)
1	1.62e-12	277.6
2	9.23e-13	288.7

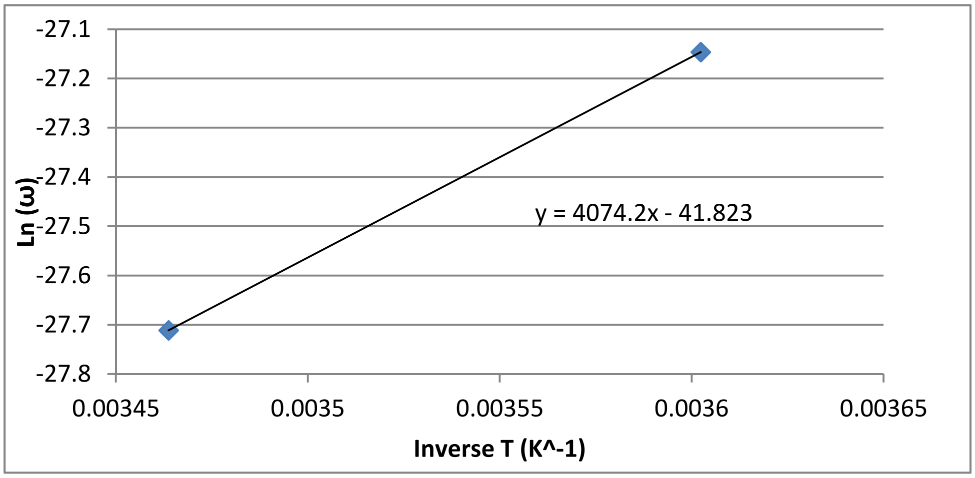


Figure 43. Arrhenius Plot of Data from TBM Loss – Literature Data

The slope and intercept information determined from the linear fit will allow the calculation of the required parameters.

For this reaction, A = 5.92e-15 kgmol/m^3·s and E_A = -3.39e7 J/kgmol.

Geometry

The domain of the pipe was modeled as follows:

Pipe Length: 100 feet.

Pipe Diameter: A baseline of 2″ and 4″ pipe diameters.

Coverage of Rust: The baseline simulations used the assumption that the entire inner wall was rusty.

Boundary Conditions:

The inlet is modeled as a mass flow inlet, with a source pressure of 60 psig and at an inlet temperature of 20°C (68°F). The incoming mixture will have the following volumetric constituents:

0 ppm di-t-butyl disulfide

2 ppm tertiary-butyl mercaptan

Balance = Methane

Simulation will occur at three flow rate conditions, corresponding to: no flow, the baseline flow rate from the Moran study of 0.05 ft^3/s or 2.94 CFM ("Mid Flow"), and a peak demand residential flowrate of 300,000 Btu/hr or 210 CFM ("High Flow") of natural gas. The pipe outlet is modeled as a passive boundary with no constraints. The pipe wall will be modeled as follows:

Material: rusted iron (thermal properties from iron pipe)

Roughness Height: 0.015"

Surface Washcoat Factor: 1.0 (this is a multiplier to the surface area)

Thermal BC: The outer boundary will be modeled as an adiabatic wall.

Fluent Model Results

Results for preliminary simulations are for the following parametric cases (Table 56):

Table 56. Parametric Table for Preliminary Simulation

Pipe I.D. (inches)\Flow Rate	No Flow	Mid Flow	High Flow
2.0	0 lb/s	2.0e-3 lb/s	3.3 e-3 lb/s
4.0	0 lb/s	2.0 e-3 lb/s	3.3 e-3 lb/s

No Flow Case

With the pipe outlet sealed, the no flow case estimates the decay rate of TBM over a simulated hour beginning with 2 ppm TBM. Assuming a first order decay, $C(t) = C_o e^{-\lambda t}$, for the single decomposition reaction, the decay rate can be estimated for each pipe size, through volume integration of the results at 30 and 60 minutes (Table 57). Di t-butyl disulfide is abbreviated as "DD".

Table 57. Results for 2 in. / 4 in. Pipe for "No Flow" Case

Species	Moles of species following duration (kgmol)			
Pipe Diameter	2 in.		4 in.	
Sample duration	0.5 hour	1 hour	0.5 hour	1 hour
TBM	5.03e-09	5.03e-09	4.03e-08	4.03e-08
DD	9.77e-15	1.55e-14	7.36e-14	1.38e-13
H_2	8.83e-15	1.11e-14	7.00e-14	1.18e-13

Calculating the decay rate, λ (h^{-1}), with the data in Table 57, the average result is

$$\lambda = 7.03\text{e-}6\ \text{h}^{-1},$$

with a standard deviation of 6.79e-7 for the range of pipe size and sample duration.

Mid and High Flow Cases

For the flowing cases, “Mid” and “High”, the transient solver runs to 10 minutes of flow time and the resulting consumption of TBM is noted as a reduction in the change in the mass-averaged TBM concentration from inlet to outlet. As shown in Figure 44, with the reaction zone shown as scaled contours with pathlines of the mean flow, both (A) the reaction zone is small and (B) the reaction rates are slow. This results in the TBM consumption rates shown in Figure 45, which as was the case in the No Flow cases, are less than anticipated based upon the Moran study. However, this was expected as the Moran study used 15psig for the inlet pressure. These simulations were performed at 60 psig.

Another point to note is the temperature dependence of the reaction rate. Since the activation energy (E_A) is negative, the reaction will initially have lower reactivity at higher temperatures. This is because the rate of adsorption of the gas molecule on a surface with temperature is inversely proportional. In other words the warmer the temperature is, the more difficult it is for TBM to adhere to the rusty surface. The variation is significant, as Figure 46 shows that the reactivity at 300K is 62% of that at 280K. These simulations were performed at 293K.

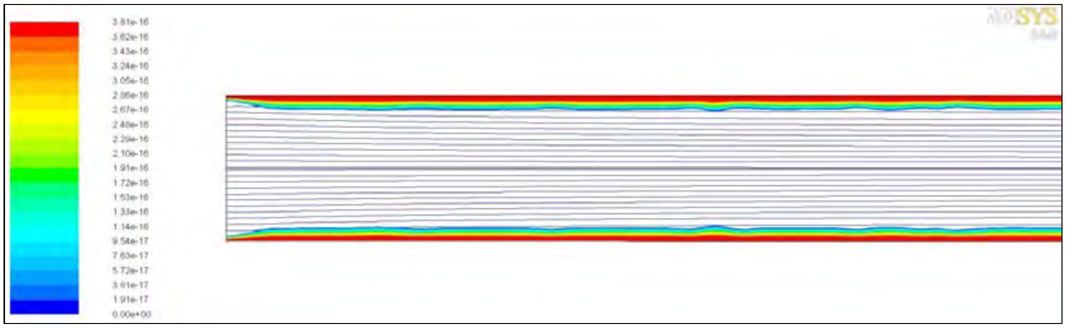


Figure 44. Contours of Reaction Rate (kgmol/m^3·K) with Pathlines for 4” Pipe Mid Flow Case

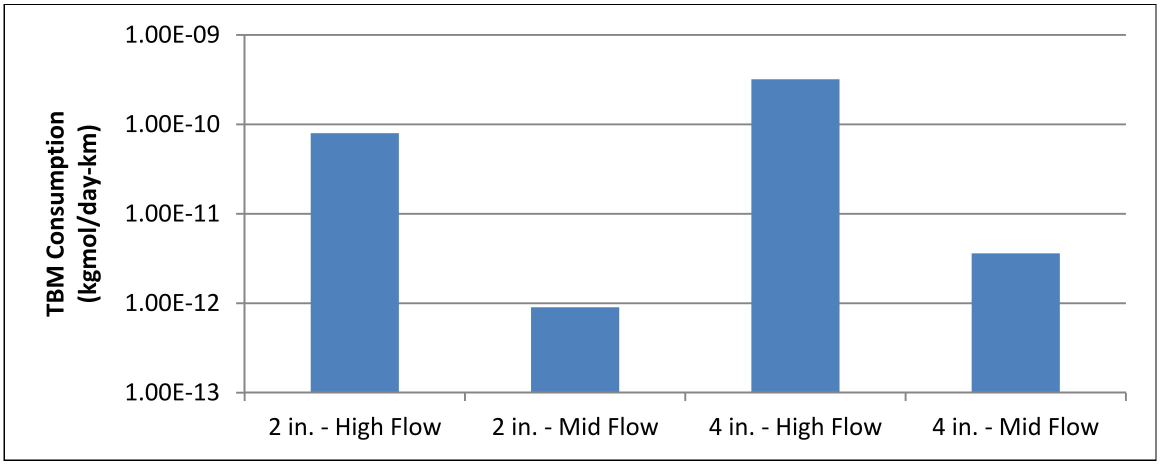


Figure 45. TBM Consumption for High/Mid Flow Cases

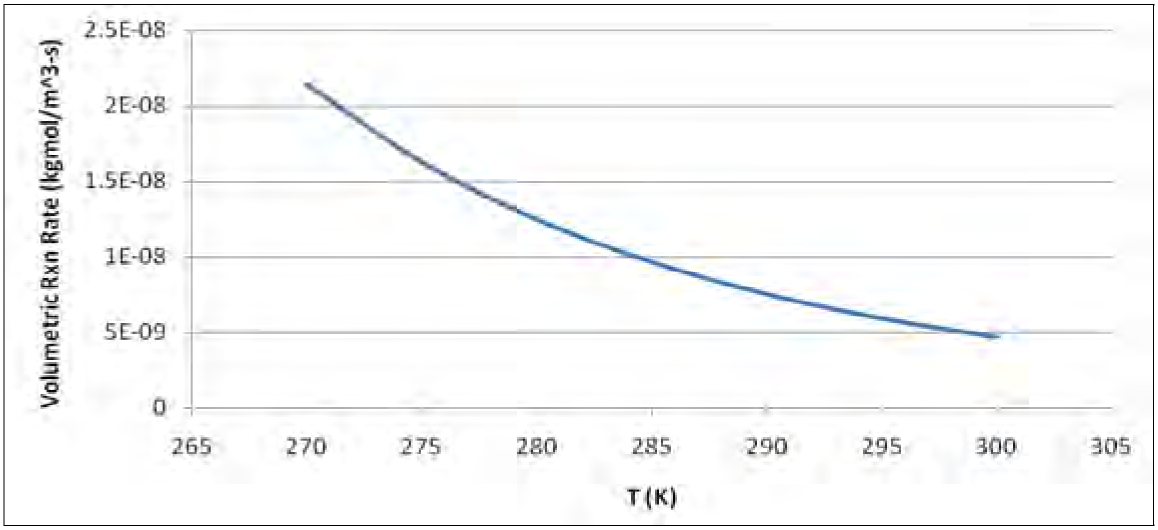


Figure 46. Reaction Rate versus Temperature for TBM Decomposition

Discussion

Following this preliminary modeling, it was postulated that the observed underestimation in simulated TBM consumption and that from the referenced *Moran* study were due to simplifications in the chemistry modeling, particularly pressure and temperature effects.

Concerning pressure effects, CFD modeling allows for inclusion of so-called "low-pressure" Arrhenius effects, through the input of separate rate constants. In the case of the preliminary modeling, the existing constants would be for this low pressure condition. For the high pressure condition, using referenced data at 150 psig versus 15 psig, unfortunately the published data does not allow for this addition. Summarized in the table below, the limited data published do not cover two temperature conditions for the elevated pressure case (all 150 psig tests are with 40°F). Therefore, while the inlet and operating pressure are changed for the subsequent simulations, they will not have a direct impact on the Arrhenius rate calculation.

Table 58. Summary of TBM Data Available from *Moran* Study

Rust Material	Pipe Pressure (psig)	Velocity (ft/s)	Temperature (°F)
Goethite	15	1	40
	15	1	60
	150	1	40
	15	10	40
	150	10	40
Hematite	15	1	40
	15	1	60

Results highlighting the impact of operating temperature are shown in Figure 47, highlighting two important results: (1) the flow rate of Mid vs. High, a 66% difference in mass flow rate, has no impact on TBM consumption at steady state and (2) as a function of the Arrhenius constants, the difference between di-t-butyl-disulfide production (half the rate of TBM consumption) at 280 and 295 K is a factor of 2.2 at steady state, for both pipe diameters. As this is purely a function of the rate constants, Figure 48 shows the calculation extended to higher temperatures. When the pressure is increased to 150 psig, all data points show no sign of variation at steady state.

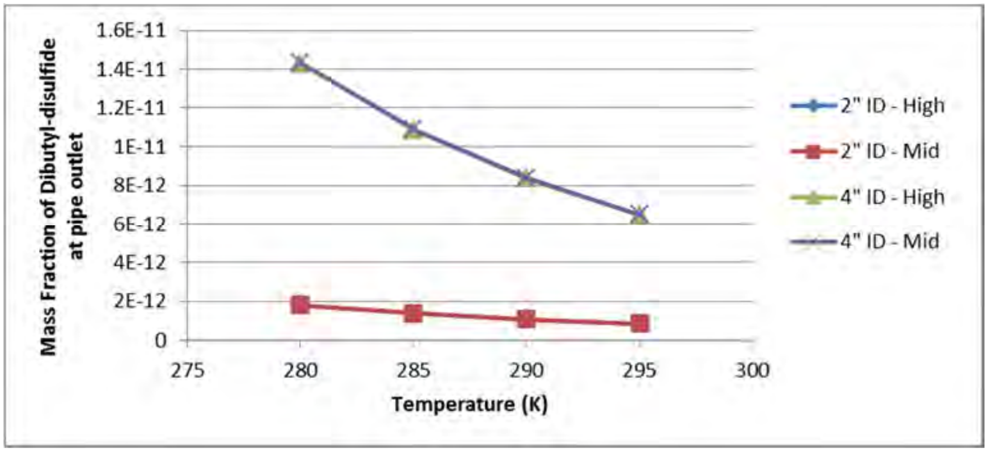


Figure 47. Effect of Temperature on TBM Consumption (Di-t-butyl-disulfide Production) at 15 psig

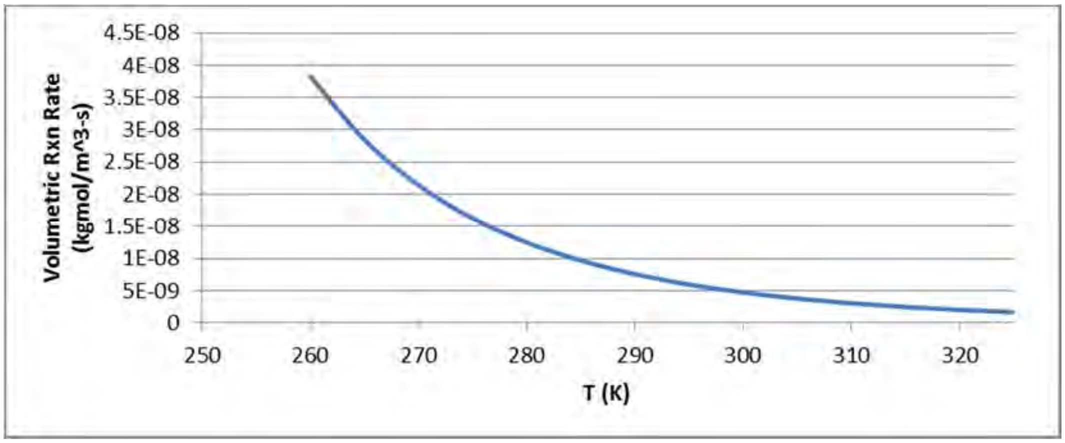


Figure 48. Calculated Arrhenius Rate for *Moran* TBM Consumption Constants

Second Modeling Effort – GTI Data Set #1

The second modeling effort used GTI lab generated data using 2" ID, 1' long pipe segments; both steel pipe and MDPE plastic pipe for TBM loss and for THT loss. From these tests, the following data in Table 59 applied. The plot of the data used to derive the Arrhenius rate law constants in steel pipe are shown in Figure 49 and Figure 50 for TBM and THT, respectively. The plot of the data used to derive the Arrhenius rate law constants for TBM and THT absorption in MDPE pipe are shown in Figure 51 and Figure 52, respectively.

Table 59. Odorant Loss Data from GTI Data Set #1

Species	Pipe Type	State Point	Steady State Consumption Rate (kgmol/s)	Temperature (°K)
TBM	MDPE	1	1.63E-11	274
		2	3.69E-11	294
	Steel	1	9.81e-12	274
		2	4.77e-11	294
THT	MDPE	1	2.13e-10	274
		2	8.43e-10	294
	Steel	1	6.52e-11	274
		2	1.63e-10	294

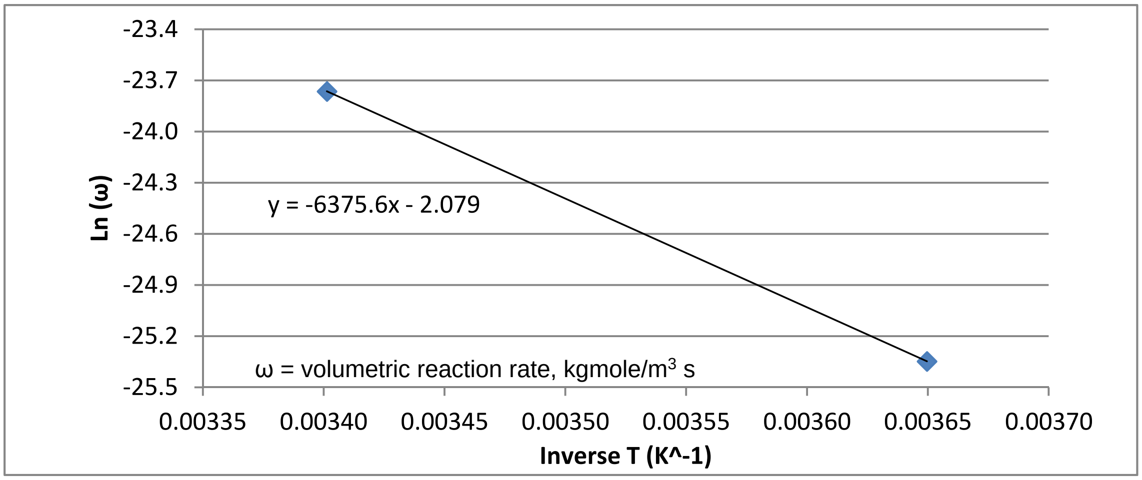


Figure 49. Arrhenius Plot of Data from TBM Loss (Steel Pipe) – GTI Data Set #1

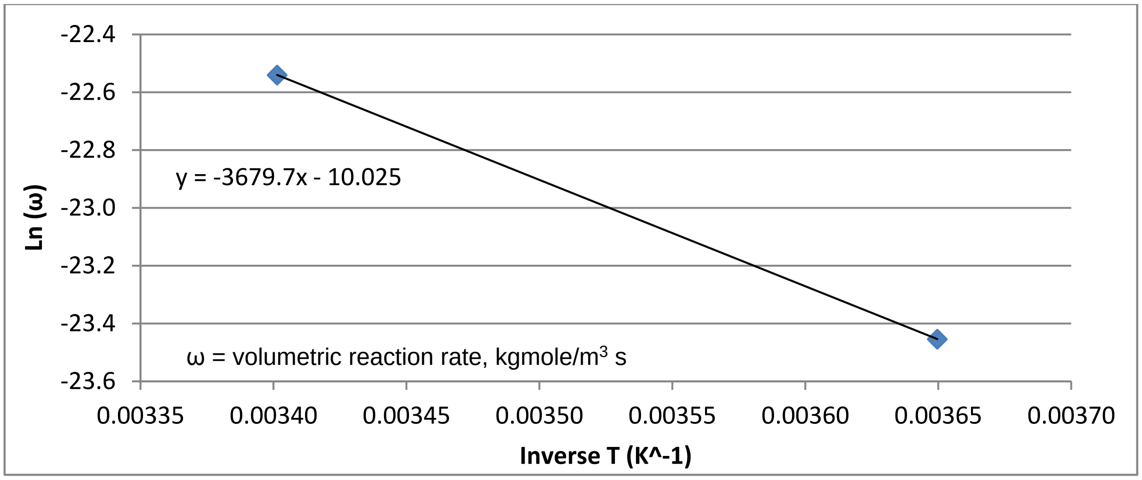


Figure 50. Arrhenius Plot of Data from THT Loss (Steel Pipe) – GTI Data Set #1

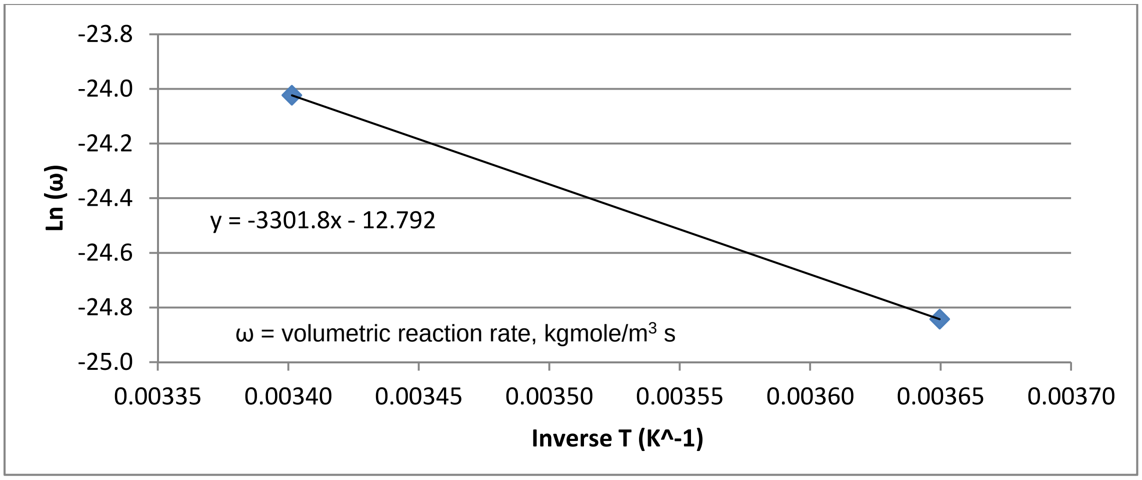


Figure 51. Arrhenius Plot of Data from TBM Loss (MDPE Pipe) – GTI Data Set #1

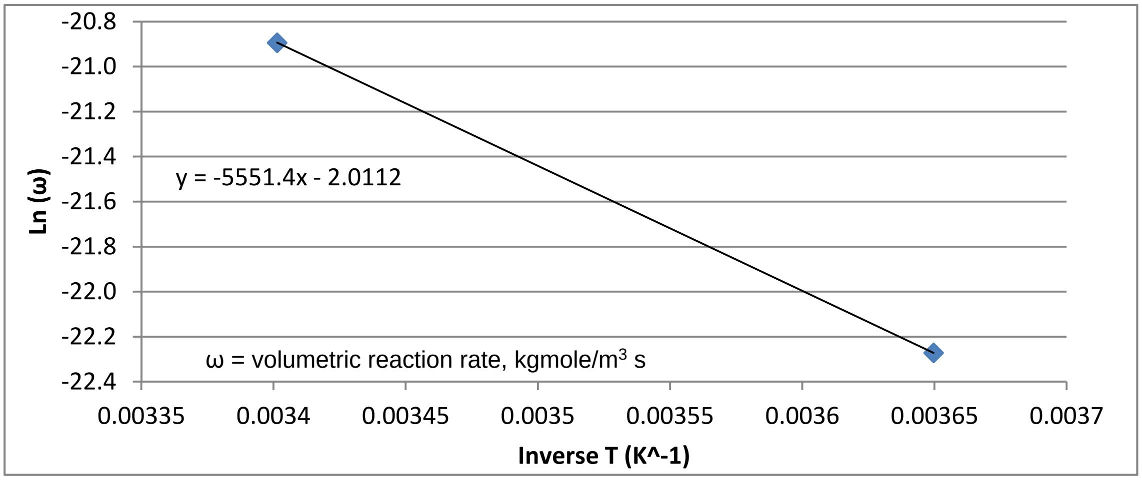


Figure 52. Arrhenius Plot of Data from THT Loss (MDPE Pipe) – GTI Data Set #1

Using the same calculation methodology as discussed previously, the values for E_A and A are shown in Table 60.

Table 60. Arrhenius Rate Law Constants from GTI Data Set #1

Species	Pipe Type	E_A, J/kgmol	A kgmol/m^3·s
TBM	MDPE	2.75e+7	4.50e-3
	Steel	5.30e+7	202
THT	MDPE	4.62e+7	217
	Steel	3.06e+7	0.0716

Geometry

The domain of the pipe is modeled as follows:

Pipe Length: The pipe is one foot long.

Pipe Diameter: 2" diameter.

Coverage of Rust for Steel Pipe Data Set: Initially, the entire inner wall will be assumed to have coverage.

Boundary Conditions

The pipe is modeled as a no flow condition (lock-in) with pressure at 60 psi and temperatures of 274°K (1°C or 34°F) and 294°K (21°C or 70°F). The gas mixture will start with the following volumetric constituents:

TBM cases:
0 ppm di-t-butyl disulfide
1.75 ppm t-butyl mercaptan
Balance = Methane

THT cases:
3.7 ppm THT
Balance = Methane

The pipe outlet is modeled as a passive boundary with no constraints. The pipe wall will be modeled as follows:

Material: steel cases: rusted iron (thermal properties from iron pipe), plastic cases: MDPE (thermophysical properties of MDPE).

Roughness Height: 0.015”

Surface Washcoat Factor: 1.0 (this is a multiplier to the surface area)

Additional Baseline Modeling with GTI Datasets

GTI data differed slightly from the *Moran* data in its collection, measurements in a static versus flowing condition, however the results were significantly different from the point of view of modeling reactions via an Arrhenius rate expression. As noted in the prior section and emphasized previously, the *Moran* study indicated that TBM consumption rates *increased* with decreasing temperatures, which was noted in the study as being a second order effect. Based on the GTI data, shown below in Figure 53 (TBM) and Figure 54 (THT), the steady-state consumption rate of both TBM and THT is shown to increase with higher temperatures, following initial dropoff effects.

Noting that the TBM concentration begins at 1.7 ppm and the THT begins at 3.7 ppm, one can see clearly the initial and significant reduction in measured odorant. For example, the THT decreases by nearly 50% at both low and high temperatures within the first four hours, a rate an order of magnitude above that observed for the balance of the sampling period. The physical reason for this behavior is due to the initial occupation of active sites within the surfaces, the consumption rate approaches an equilibrium value once the active sites are initially occupied. It is this “quasi-equilibrium” rate that one can model with an Arrhenius rate expression, the initial occupation of active surface sites and its resultant steep decline in odorant must be modeled directly through separate means.

Also of note is the comparison of overall odorant loss between the steel and MDPE material in Figure 53 (TBM) and Figure 54 (THT). The total loss of odorant with the lightly rusted steel pipe occurs faster at the higher temperature. The total loss of odorant with the MDPE pipe is also faster at the higher temperature. This latter data is indicative of an absorption effect occurring where the higher temperature is promoting absorption of the TBM into the plastic matrix. At the lower temperature the impact of both phenomena is less.
Because PE is a nonpolar molecule, it is a very poor barrier to nonpolar hydrocarbons such as the odorant molecules.

The opposite phenomenon is occurring with THT. At the higher temperatures the overall final odorant losses are less than at the lower temperature. This points toward a surface effect like adsorption which is impacted significantly by temperature. Condensation on a surface will be promoted by lower temperature.

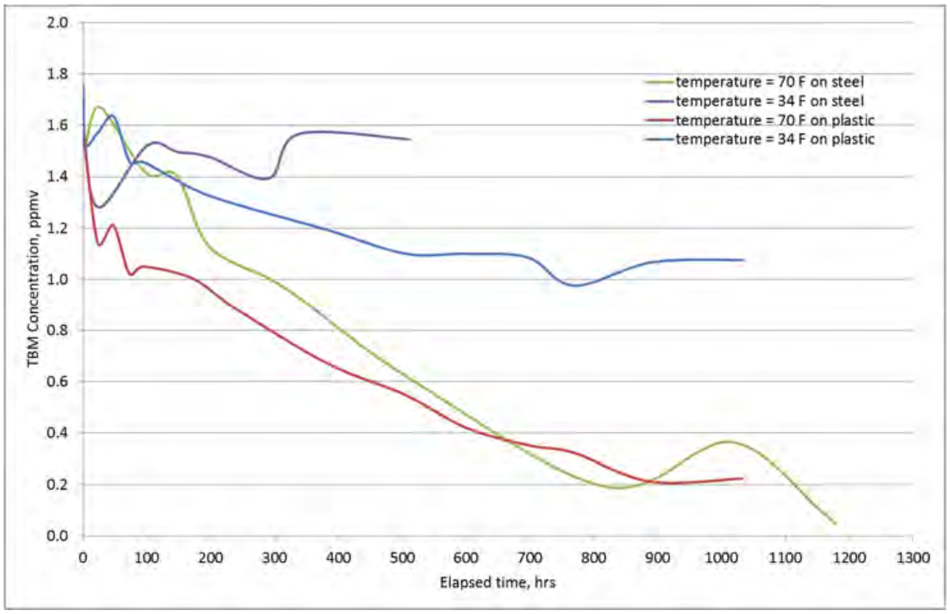


Figure 53. Summary of GTI Datasets – TBM Odorant Concentration vs. Time

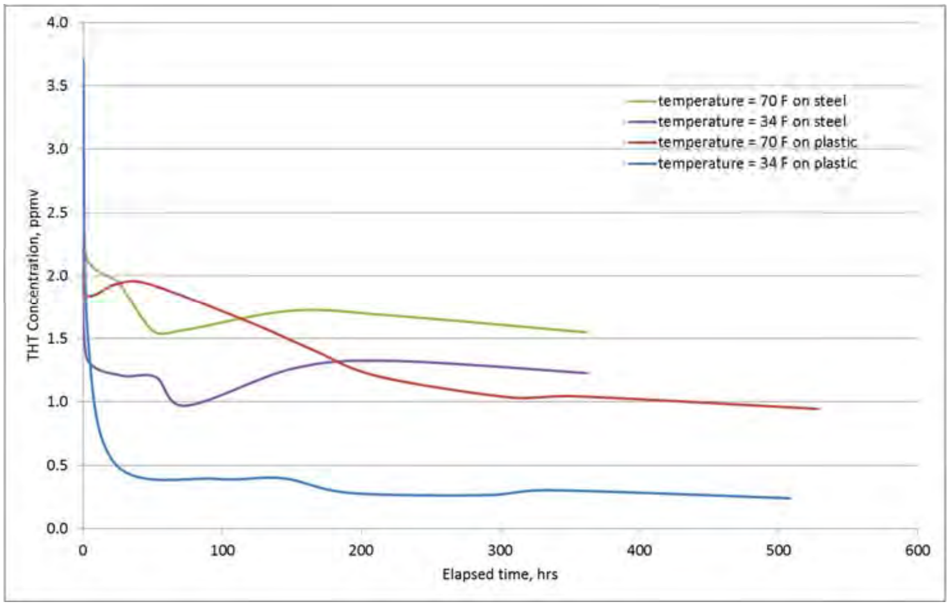


Figure 54. Summary of GTI Datasets – THT Odorant Concentration vs. Time

As the temperature sensitivity identified by the *Moran* modeling data highlighted, partially due to the limited nature of the effects of pressure, initial modeling of the GTI data found that an additional temperature dependency was required with the added constant *b*, as shown in the formula below. Through initial estimation, a value of *b* = 0.85 was used.

Equation 6: $$\dot{\omega} = T^b A \cdot exp^{-E_A/RT}$$

Baseline Modeling with GTI Datasets: TBM-Steel and THT-MDPE

As can be seen in Figure 55, summarizing the odorant consumption for the four transient, no-flow CFD simulations, the initial steep drop-off is not modeled, thus not observed, and is postulated to be due to the initial occupation of active surface sites. The comparison of experimental datasets to modeling results is shown in Figure 56 and Figure 57, where it can be seen that with the exception of the initial drop-off in TBM and THT, the rate of consumption (slope) for this initial period of 200 hours shows good agreement.

Considering the case with the poorest agreement, the THT consumption case at 274 K, it can be seen that the initial drop-off from the occupation of active surface sites and other non-steady initial effects results in an over 80% decrease in odorant within the first 20 hours. To highlight the agreement between the Arrhenius-based modeling and measured data after this period, the THT consumption is scaled a second time from the beginning of the 24th hour, which shows excellent agreement with the modeled case.

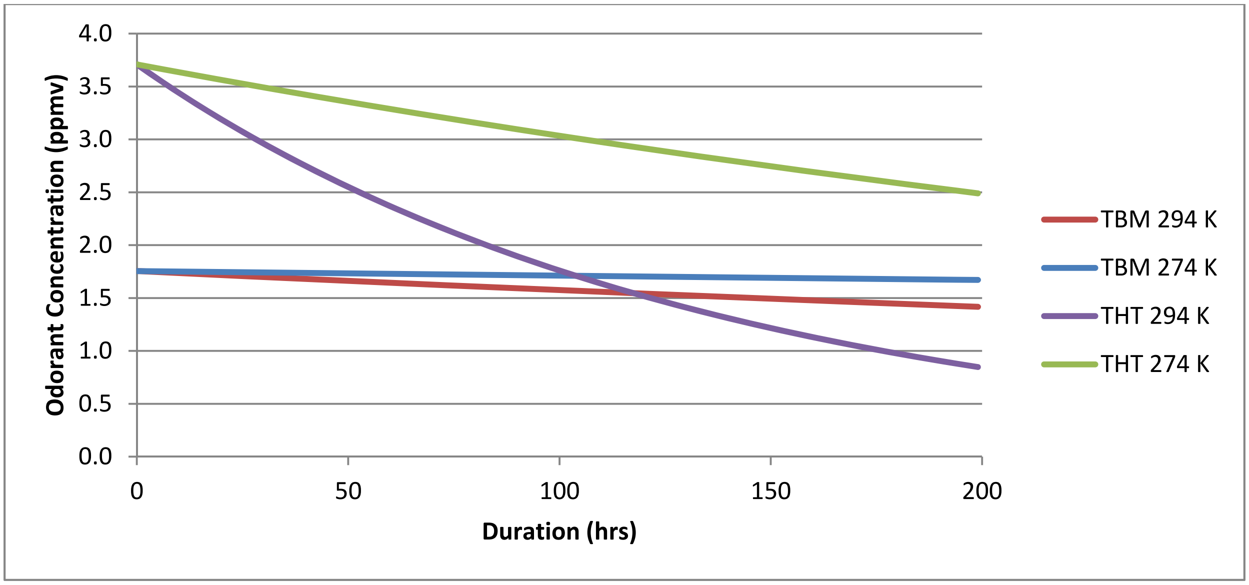


Figure 55. Summary of Modeled Data – CFD Odorant Consumption (TBM & THT-MDPE)

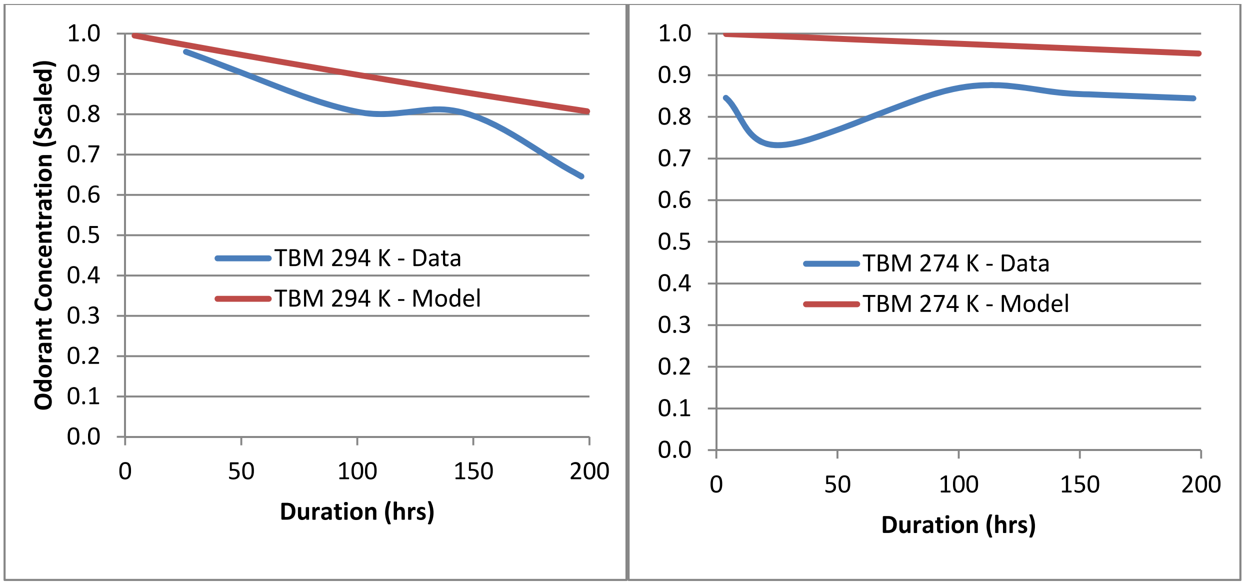


Figure 56. GTI Data vs. Modeling Results – TBM Consumption – Steel Pipe

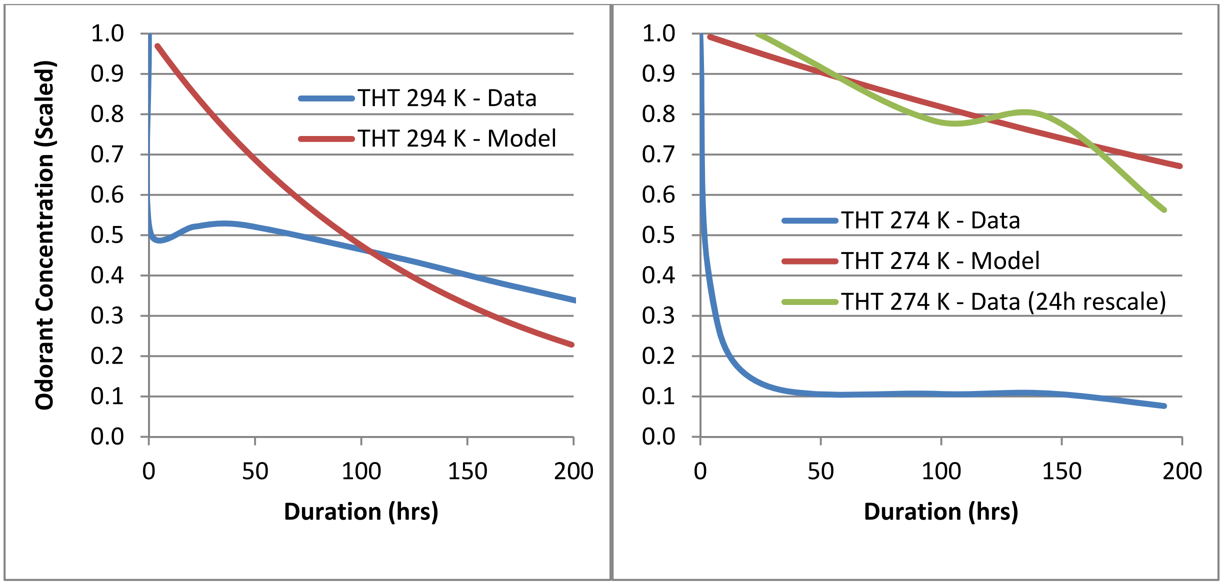


Figure 57. GTI Data vs. Modeling Results – THT Consumption - MDPE

Baseline Modeling with GTI Datasets: THT-Steel

In the case of the adsorption of THT onto steel pipe[1], the use of the temperature exponent *b* in the Arrhenius expression was also employed to obtain better baseline information against the experimental data. The impact is shown at T = 274°K and T = 294°K in Figure 58 and Figure 59 respectively.

- no added temperature dependency (*b* = 0) underestimates consumption,
- *b* = 1.15 over estimates consumption, and
- *b* = 1 offers a reasonable fit for both temperatures.

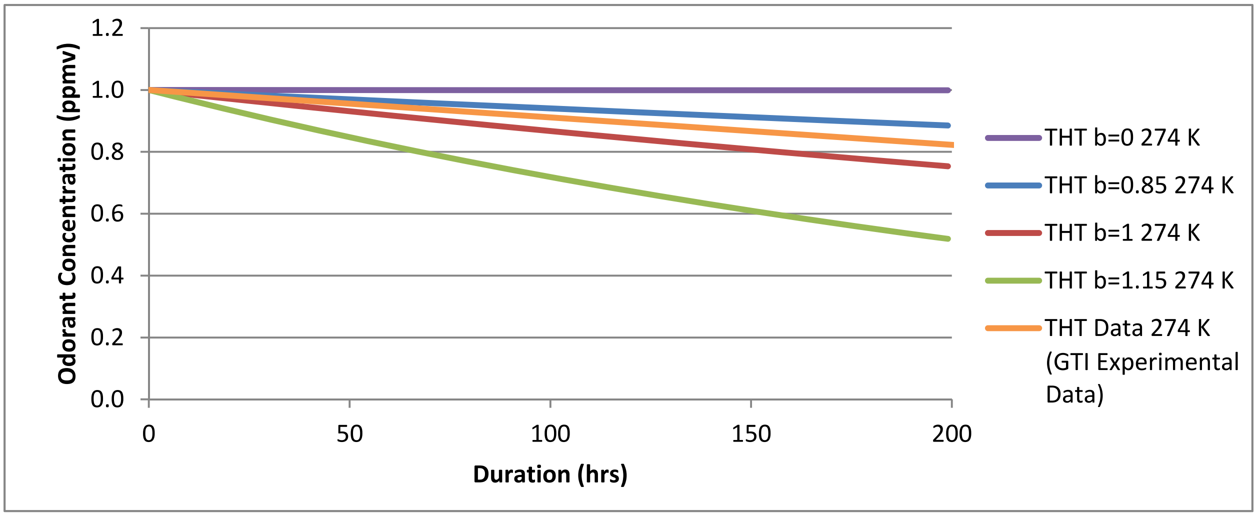


Figure 58. Impact of Exponent *b* on THT Loss in Steel Pipe - 274 K

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[1] THT in the presence of rusted steel pipe can also chemically degrade as does TBM through direct oxidation; however the primary mechanism of odorant loss is direct adsorption.

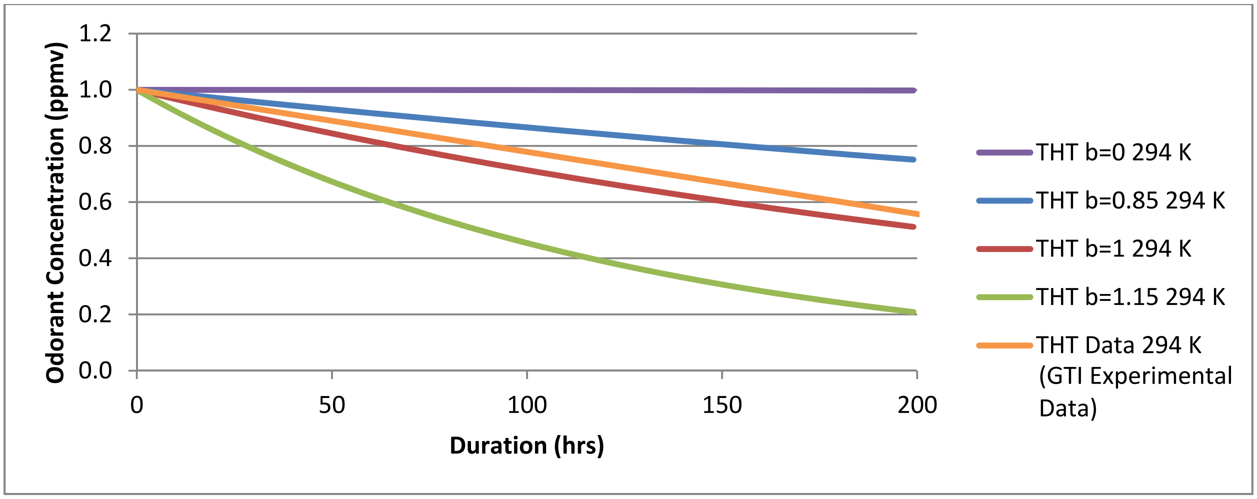

Figure 59. Impact of Exponent *b* on THT Loss in Steel Pipe - 294 K

Baseline Modeling with GTI Datasets: TBM-MDPE

Preliminary results, summarized in the following two figures suggested that the initial selected values of the temperature exponent *b* used were insufficient to match the GTI experimental datasets, due in part to the much smaller pre-exponential constant *A* from this dataset versus that of the previously evaluated datasets. This is a reflection of the much slower absorption period of TBM with plastic compared to the other odor loss experiments. That said, the disagreement with results below shows that the early absorption effects are stronger in relation to the longer term odor loss rate, thus a more aggressive temperature constant will be needed and it is possible that a multi-step global mechanism may be required to describe this odorant loss pathway.

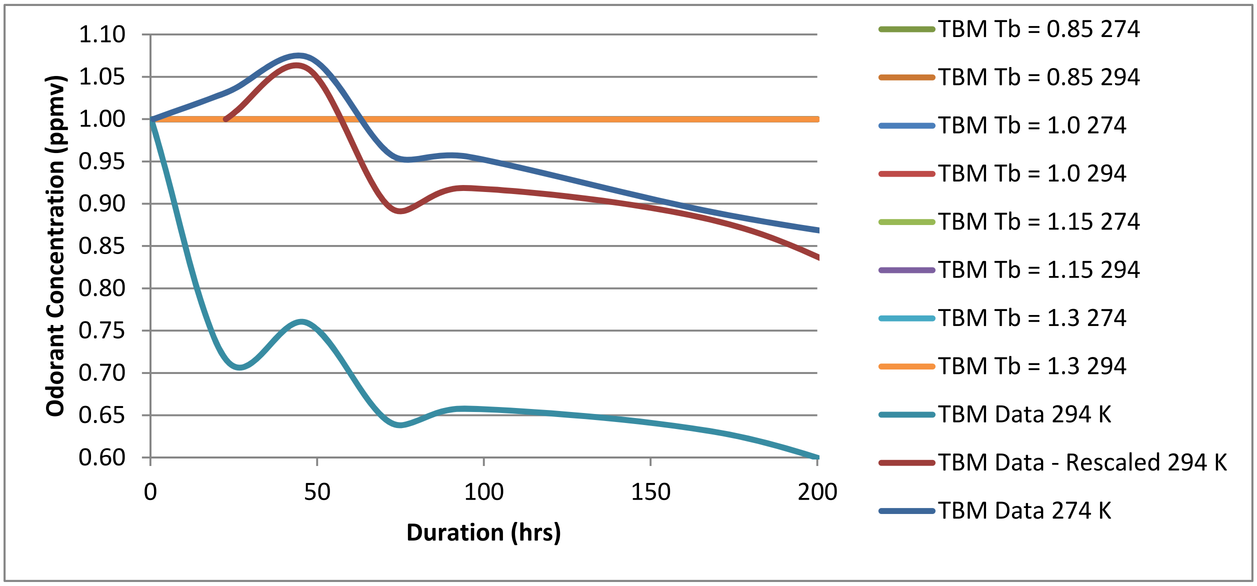

Figure 60. Full Comparison of TBM Loss with Plastic

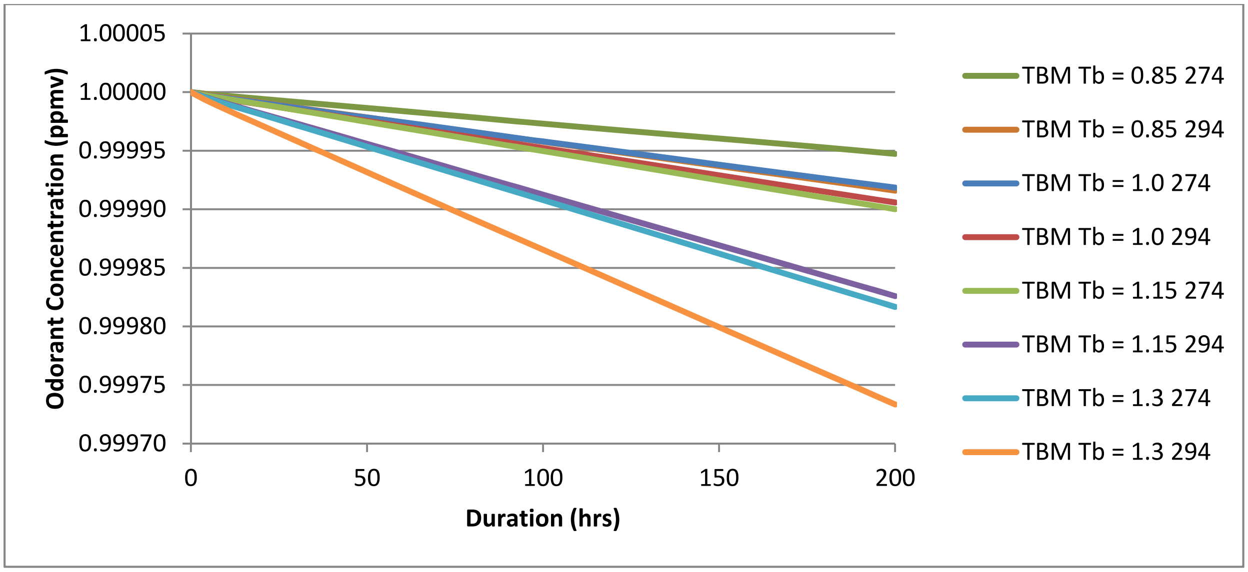

Figure 61. Modeling Results of TBM Loss with Plastic – Zoomed In

As a result, temperature exponents *b* in a higher range than previously tried were examined. Whereas 0.85 < *b* < 1.3 was previously modeled, 1.4 < *b* < 2.0 is modeled in this case. As the data show, in Figure 62, *b* = 1.4 offers a reasonable fit over the temperature range and time period analyzed. In the case of the GTI data at 294°K, the data is scaled to neglect the initial occupation of active sites during the first data point, more appropriately represented by the quasi-steady state simulation. Neglecting the balance of values of *b* simulated greater than 1.4, which are shown to overestimate odorant loss, Figure 63 shows the comparison of *b* = 1.4 versus the data, with and without scaling. This value of 1.4 is an appropriate fitting constant for TBM loss in plastic pipe.

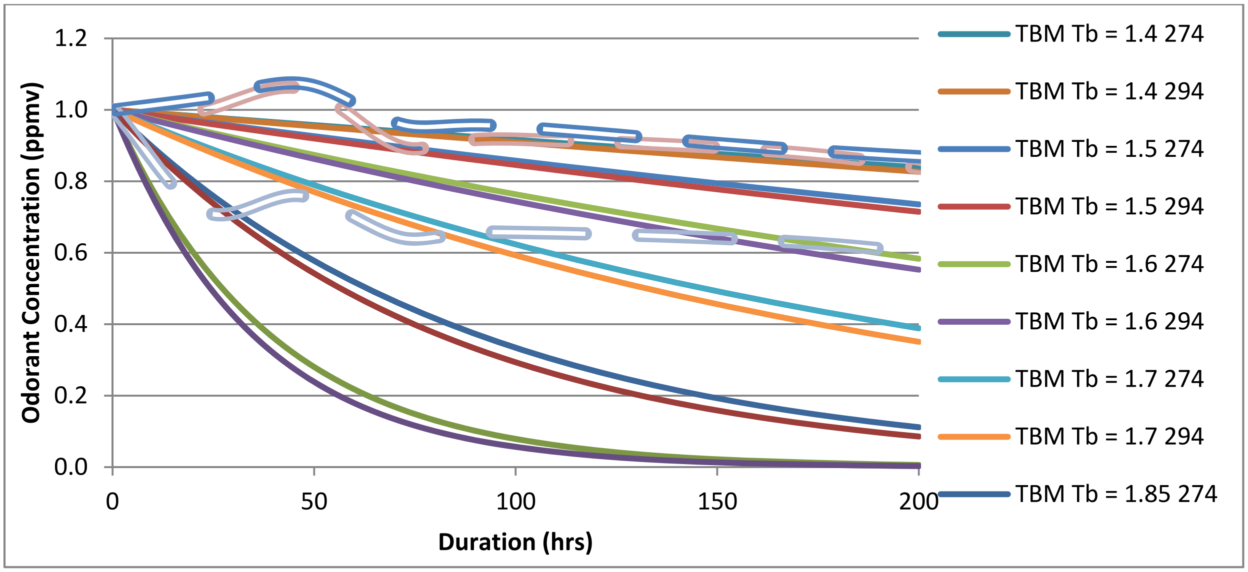

Figure 62. Full Comparison of TBM Loss with Plastic - Higher Range of *b*

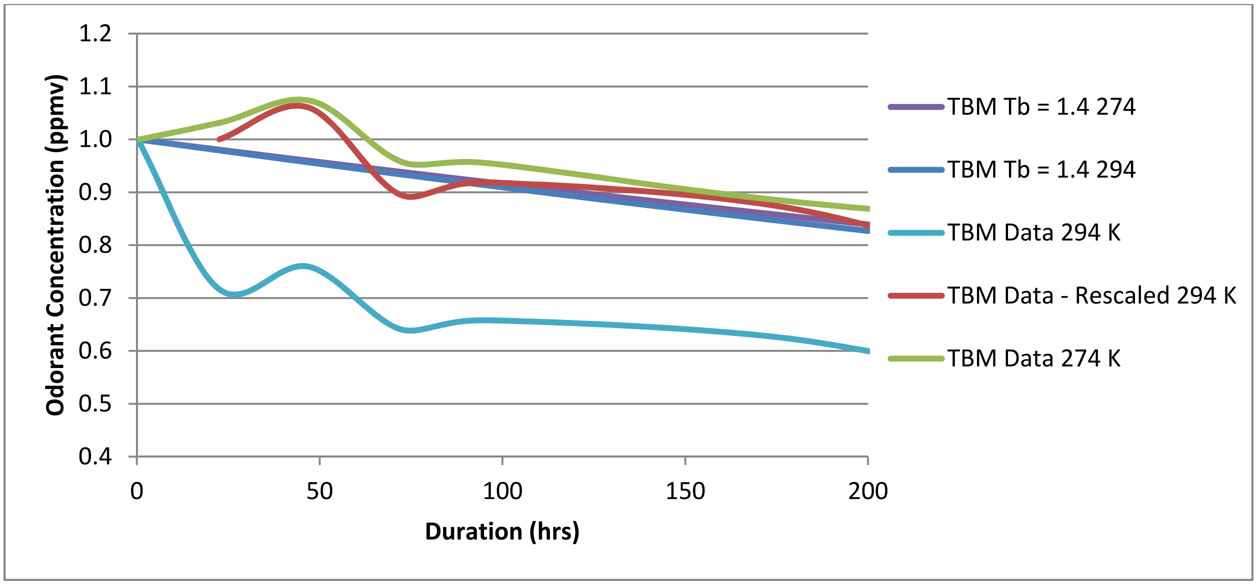

Figure 63. Curve Fit of *b* = 1.4 vs. GTI Data Set #1

General Conclusions

In the case of the baseline model against the *Moran* study, the data was shown to be incomplete from the perspective of assessing the pressure-dependency of odorant consumption reactions. In addition, it was skewed in the treatment of second-order temperature effects, in that the odorant consumption has an inverse relationship to temperature. The influence of temperature was explored with the *Moran* data, and later prompted the added temperature dependency in the Arrhenius rate expression.

From the GTI datasets, a good correlation was observed for odorant consumption rates when the added temperature dependency is included. Table 61 summarizes the data obtained in the second model effort.

Table 61. Summary of Arrhenius Rate Expression Parameters Values from GTI Data Set #1

Species	Pipe Type	Arrhenius Rate Expression Parameters for: $\dot{\omega} = T^b A \cdot exp^{-E_A/RT}$		
		E_A J/kgmol	A kgmol/m^3·s	*b*
TBM	MDPE	2.75e+7	2.78e-6	1.4
	Steel	5.30e+7	1.25e-1	0.85
THT	MDPE	4.62e+7	1.34e-1	0.85
	Steel	3.06e+7	4.43e-5	1.0

Modeling Field Conditions

The goal of this task was to validate the original models through a series of physical tests on pipeline segments and/or systems. The original option as described in the proposal involved piggy backing on an already operating line at one of the stakeholder companies.

However, discussions with project stakeholders suggested that there were many issues regarding the field testing of long lengths of piggy backed pipe initially proposed to be performed at company sites. These issues include the extensive amount of time, work and cost that would be required for this type of testing. None of the other project participants wanted to piggy back any pipe onto their existing pipelines.

GTI felt that the best solution was to do odorant analysis during an actual natural gas pipeline installation and/or conditioning project. This would offer the best compromise on cost and time while providing in situ real life measurement of odorant activity. Monitoring or collection of gas samples could be conducted at selected sampling points in a pipe or system (Figure 64) during an actual pickling operation as it is being conducted by a participant company.

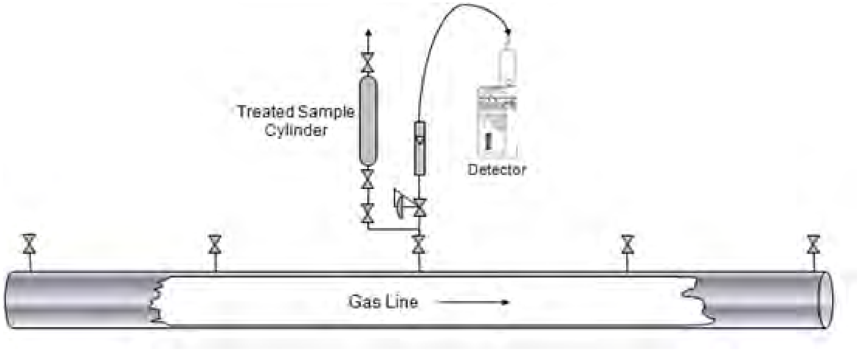

Figure 64. Example Setup for Monitoring Odorant Levels during an Actual Natural Gas Pipe Pickling/Conditioning Project in the Field

However, as the final task progressed, economic factors delayed many significant new construction projects for the companies contacted. According to U.S. Census Bureau data, total construction and new home construction was at an all-time low as the project began and only now is beginning to recover (Figure 65). This lack of building made it difficult to obtain field test data from companies otherwise willing to participate.

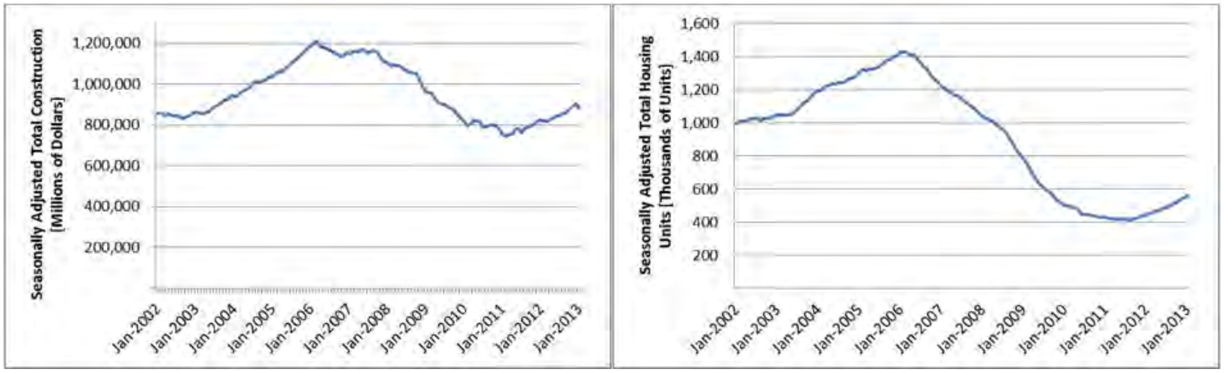

Figure 65. U.S. Census Bureau Data for Construction

Several companies did supply field data for samples taken during line commissioning. Unfortunately, none of the construction project timelines went as expected, due to leaks and operational issues. Too many variables were present making it impossible to use the data to correlate to the lab models.

In retrospect, the best solution would have been to construct a flowing test loop, with easily replaced pipe sections and sulfur monitor stations. This was investigated early in the project but due to the high cost, was abandoned in favor of the sampling during a commissioning event.

The best field case data is presented in Case #2, but with no exploration as to its correlation with the model data.

Modeling with Field Datasets: TBM-THT-Steel

Modeling of Field Conditions Case #1

Using the methodology outlined previously, the following case was modeled:

Pressure: 10 psig

Temperature: 60°F

Pipe Outer Boundary: Adiabatic

Pipe Material: Rusted Iron Pipe

Pipe Diameter: 8 in.

Pipe Length: 1/8 mile[2]

Flow case: Lock-up (no flow) for 3 days

Initial Concentration: 125 ppmv TBM, 125 ppmv THT

Using the Arrhenius parameters from this study for TBM and THT loss in rusted iron pipe, based upon GTI data, and including values of *b* of 0.85 and 1.0 respectively, the resulting concentrations of TBM and THT after 4 hours are approximately the same, around 120 ppmv, and after 3 days fall to 75 ppm and 13 ppm respectively (Figure 66).

This is contrary to expected experience and to the limited field data obtained for Case #1 as shown in Table 62. (Data was provided as peak areas from a GC analysis. Odorant levels were approximated from the limited dosing information provided.) THT is expected to be much more stable than TBM, and the TBM is expected to fade very quickly.

Table 62. TBM and THT Field Data for Case #1

Time, hours:	0	2	3.5	3.8	4	4.3	4.5
% TBM	0.0	0.0	0.0	4.3	0.7	1.5	1.1
% THT	0.0	0.0	0.0	95.7	99.3	98.5	98.9

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[2] Case is 2 miles, however the effect of length on concentration for the adiabatic pipe case is negligible.

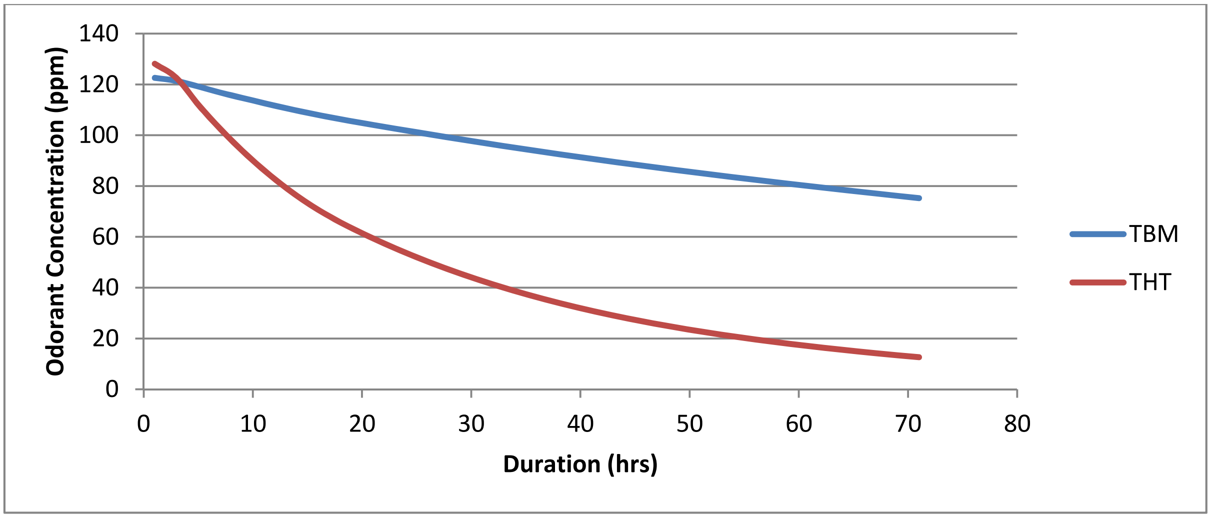

Figure 66. TBM and THT Odorant Loss for Field Case #1

Modeling of Field Conditions Case #2

Using the methodology outlined previously, the following case was modeled:

Pressure: 310 psig

Temperature: 81°F

Pipe Outer Boundary: Adiabatic

Pipe Material: Rusted Iron Pipe

Pipe Diameter: 20 in.

Pipe Length: 1/8 mile[3]

Flow case: Lock-up (no flow) for 2 days

Initial Concentration: 3.33 ppm odorant; 1.08:1 TBM:THT

The simulation was performed in a similar to Field Case #1, using the Arrhenius parameters from this study for TBM and THT loss in rusted iron pipe (values of *b* of 0.85 and 1.0 respectively). With a projected combined odorant concentration of 1.55 ppm after 2 days, this simulation case may be overestimating odorant loss. As shown in the simulation of Field Case #1, THT loss outpaces TBM loss.

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[3] Case is much longer, however the effect of length on concentration for the adiabatic pipe case is negligible.

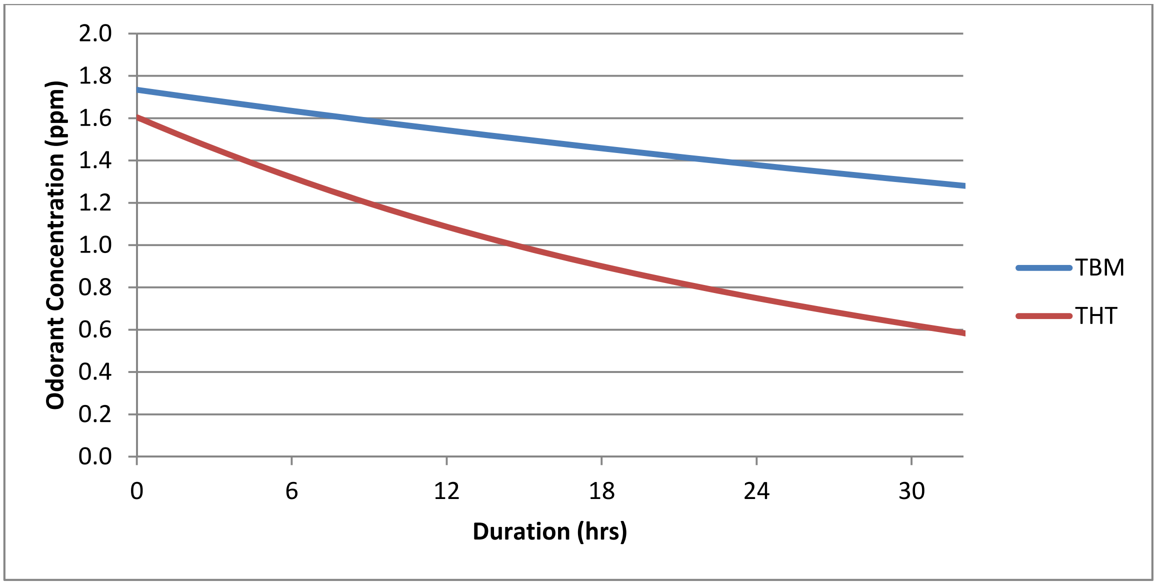

Figure 67. TBM and THT Odorant Loss for Field Case #2

This is again contrary to expected experience and to the limited field data obtained for Case #2.

In both Case #1 and Case #2, the THT odorant loss is significantly over estimated. However, the TBM odorant loss is over estimated also, to a lesser extent. It is expected that this could be happening for two reasons:

- **Modeling of active/inactive sites -** As mentioned previously, modeling does not include direct modeling of active/inactive surface sites, whereby an adsorbed species will physically occupy a surface site of rusted interior pipe. As such, when using rate constants and fitting parameters for the loss of individual odorant species, this combination of species allows for "double-counting" of active sites. For example, if TBM was the only odorant its projected concentration after 2 days is 2.63 ppm, close to that of lab measurements of 2.72 ppm (calculated from information in the original GTI lab data sets).

- **Assumption of isothermal uniformly rusted (active) interior surfaces -** Rate constants and fitting parameters were derived for short sections of pipe with uniformly rusted interiors under controlled temperature conditions. As actual coverage of rust is not expected to be uniform and temperatures will drop below 81°F, the modeling bias is to overestimate odorant loss.

Table 63 lists the information that could be extracted from the available field data for Case #2. The THT odorant, as expected again, is much more stable than the TBM. The complicating elements include the fact that embedded in the pipe run was a 1300 feet length of previously conditioned pipe that had been in service for two years. In addition, the original plan was to bring the whole line up in one day and then put it in service the next day. However, for an unknown reason the construction crew did not make the final tie in at the end of the line for a couple weeks after pressuring it up. As a result some gas fed through a couple of regulator stations.

Table 63. Field Data for Case #2

DAY 1	TBM, ppmv	THT, ppmv	Comments
Gas feed	1.73	1.60	10 oz odorant added
7,700 ft	0.04	0.05	With N_2 purge, 12 oz odorant added
17,200 ft	0.30	2.24	2 hours later, 11 oz odorant added
25,600 ft	5.22	10.68	4 hours later, 25 oz odorant added
37,050 ft	0.03	1.04	
45,100 ft	0.21	3.17	
DAY 2			
7,700 ft	0.04	1.47	flowing gas
45,100 ft	0.03	2.69	no flow
DAY 4			
17,200 ft	1.05	1.51	
DAY 12			
45,100 ft	0.05	2.41	no flow (locked in)
45,100 ft	0.02	1.40	7000 MCF/day
DAY 13			
45,100 ft	0.71	1.66	17000 MCF/day
DAY 14			
45,100 ft	0.48	1.54	16000 MCF/day
DAY 15			
45,100 ft	0.70	1.60	
Gas feed	1.70	1.45	

Due to the overconsumption of odorant, especially THT, from the simulated field sites, consideration was given to perform a laboratory test that would yield the reaction rates for the competition of TBM and THT to the active sites. Unfortunately, the equipment to dose the reactors had been disassembled several months earlier. The parts were reassembled but the resulting data set was poor. In all cases, the data led to negative Activation Energies. The prior four datasets for TBM and THT in plastic and steel individually all had positive Activation Energies.

Modeling with Field Datasets: THT-Plastic

THT in plastic was one of the field data sets that we thought would be available, but the field engineers were unable to take field samples due to lack of resources and manpower. The original model data is presented as found.

Modeling of Field Case #3

Using the methodology outlined in this report, the following case was modeled:

Pressure: 60 psig

Temperature: 60°F

Pipe Outer Boundary: Adiabatic

Pipe Material: MDPE (Plastic)

Pipe Diameter: 2 in.

Pipe Length: 1 mile

Flow case: 0.02MMCFH

Initial Concentration: Starting with 100% CH_4, dosed with 4 ppm odorant, THT at inlet

Similar to the prior recreation of *Moran* data, this flowing case is simulated as steady state. As the Arrhenius parameters derived for odorant loss incorporate the dynamics of occupying active surface sites without the explicit modeling of active site occupation (i.e. the desorption and adsorption reaction is not directly modeled), the transient effects of initial site occupation are not captured. This is especially important for THT loss within plastic pipe as seen with modeling of lockup cases, where agreement is seen with long term odorant loss rates when scaled to exempt these initial effects (e.g. Figure 57). To verify that this assumption is valid, a transient case was run to observe how quickly steady state consumption is achieved.

Using the Arrhenius parameters from this study for THT loss in MDPE, a transient model with velocity boundary conditions is used. Average velocities are rather high at 79 m/s, which limits the residence time of the THT at the pipe interior surface. After verifying that the THT loss behaves linearly with distance for isothermal cases, the odorant loss is extrapolated to longer distances. Results summarized in Table 64 show that roughly 1.85 ppm of THT odorant is consumed per mile, with all odorant expected to be consumed within 2.1 miles. This may be conservative as mentioned previously, as this does not include initial site occupation, however with steady state reached rapidly in flow-time, in less than 10 minutes; this effect is expected to be minimal for a constantly dosed flowing case.

Table 64. Calculations from Field Case #3

Odorant loss per (ppm)		Distance to lose 4 ppm odorant (miles)
1 mile	2 miles	
1.85	3.70	2.1

Modeling of Field Case #4

Using the methodology outlined in this report, the following case is modeled:

Pressure: 60 psig

Temperature: 70°F

Pipe Outer Boundary: Adiabatic

Pipe Material: MDPE (Plastic)

Pipe Diameter: 2 in.

Pipe Length: 100 Ft. (all modeled)

Flow case: Lockup

Initial Concentration: THT at 100 ppm

After twelve hours, the concentration of THT in the locked in pipe falls to 30% of the original concentration (Figure 68). This case was meant to simulate construction of new service lines where flowing gas did not directly occur because tie-ins to residential areas were not immediately added to keep gas flowing.

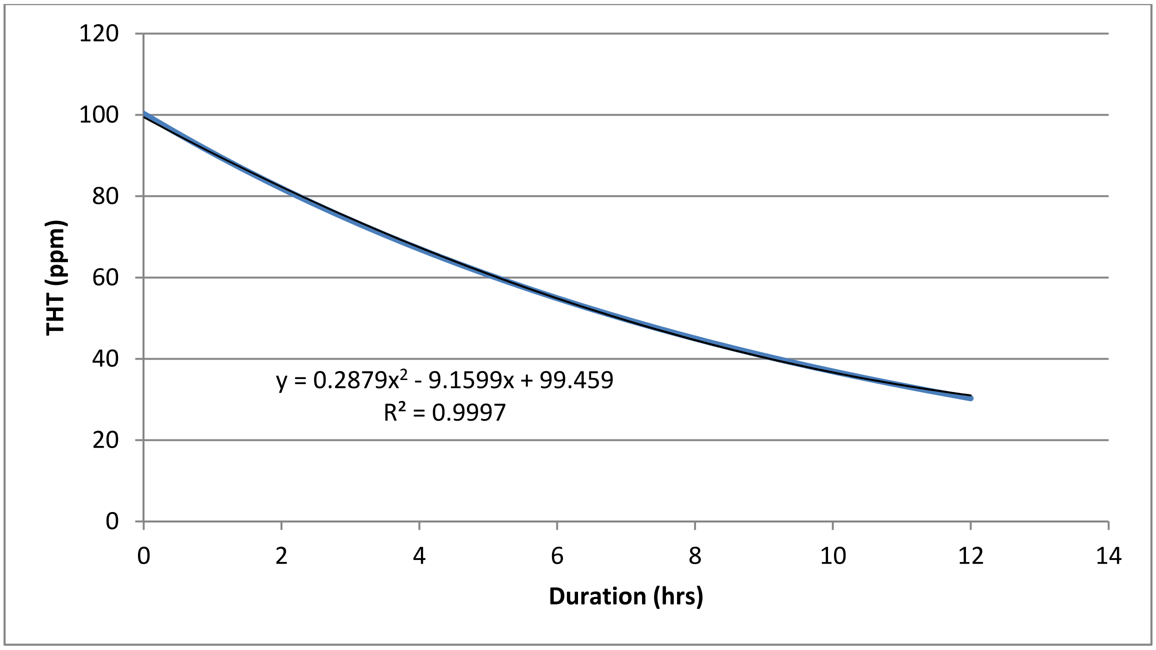

Figure 68. THT Loss for Field Case #4

Additional Field Sites

Late in the project another company offered to collect samples during a new installation effort. GTI offered to either visit on site or supply inerted cylinders for field personnel to use. The company chose the latter option, but unfortunately due to manpower issues and other responsibilities was not able to collect any samples.

New Ansys Fluent Modeling

Motivation

With revised laboratory data for selected cases, the general kinetic computational fluid dynamics (CFD) models were revised from previous efforts and, in the case of the TBM-steel pipe model, substantially improved in scope and detail. Concerning the latter, a new methodology was selected to develop a multi-step consumption model for TBM in steel pipe, including tracking of active sites (adsorption/desorption). In the end, using experimental data and verified through targeted modeling, all Arrhenius Rate parameters were derived for modeling a general case.

An important aspect of this revised modeling is the shift from the use of a thin volumetric reaction zone to surface chemistry on the interior wall itself, requiring a shift in both how parameters are treated and which submodels are deployed.

Considerations for Steel Pipe

As part of the new modeling effort, a more complex approach to the decomposition of TBM in the presence of rusted steel was derived and tested. Unlike the adsorption of THT to plastic pipe, a concern with simplifying the adsorption, then reaction, of TBM on rusted steel is that it (a) does not accurately take into account the accounting of available active surface sites, thus ignoring competitive adsorption, and (b) loses accuracy in grouping the various adsorption/desorption steps with the reaction step. The consumption of TBM into di-tert butyl disulfide in steel pipe was modeled following this simplified reaction series:

Adsorption:

$(CH_3)_3CSH(g) + Fe_2O_3{\cdot}nH_2O\ (s) \rightarrow (CH_3)_3CSH\ (s)$

$(CH_3)_3CSH(g) + FeO(OH)\ (s) \rightarrow (CH_3)_3CSH)_3\ (s)$

Reaction:

$2\ (CH_3)_3CSH(s) + 3\ Fe_2O_3{\cdot}nH_2O\ (s) \rightarrow (CH_3)_3CS\text{-}SC(CH_3)_3\ (s) + 2\ Fe_3O_4\ (s) + (n+1)\ H_2O\ (s)$

$2\ (CH_3)_3CSH(s) + 6\ FeO(OH)\ (s) \rightarrow (CH_3)_3CS\text{-}SC(CH_3)_3\ (s) + 2\ Fe_3O_4\ (s) + 4\ H_2O\ (s)$

Desorption:

$(CH_3)_3CS\text{-}SC(CH_3)_3\ (s) \rightarrow (CH_3)_3CS\text{-}SC(CH_3)_3\ (g) + Fe_3O_4\ (s)$

$H_2O\ (s) \rightarrow\ H_2O\ (g) + Fe_3O_4\ (s)$

Grouping "rust" into a single category, indicated as "Fe" separate by active or inactive states, one may reduce this into a 4-step mechanism with stoichiometric coefficients adjusted for consistency:

1) $TBM(g) + Fe(s)_{active} \rightarrow TBM(s)$ [Adsorption]
2) $TBM(s) + Fe(s)_{active} \rightarrow 0.5\ DTBD(s) + 2\ H_2O(s) + Fe(s)_{inactive}$ [Reaction]
3) $DTBD(s) \rightarrow DTBD(g) + Fe(s)_{inactive}$ [Desorption, odorant]
4) $H_2O(s) \rightarrow H_2O\ (g) + Fe(s)_{inactive}$ [Desorption, water]

Desorption Model

Based on the simple and commonly used Languir Model, a parameter θ can be assumed for the *competitive adsorption* of TBM vs. water vapor, which estimates the fraction of covered surface sites, at equilibrium for a given temperature (i.e. $K_{eq} = f(T)$):

Equation 7:
$$\theta_{TBM} = \frac{K_{eq}^{TBM} p_{TBM}}{1 + K_{eq}^{TBM} p_{TBM} + K_{eq}^{w} p_{w}}; \ \theta_{w} = \frac{K_{eq}^{w} p_{w}}{1 + K_{eq}^{TBM} p_{TBM} + K_{eq}^{w} p_{w}}$$

For all available surface sites, S_o:

Equation 8
$$\theta_w = \frac{\left[H_2O_{(s)}\right]}{\left[S_o\right]}; \theta_{TBM} = \frac{\left[TBM_{(s)}\right]}{\left[S_o\right]}$$

Based on the definition of K_{eq} for species *i,* the adsorption and desorption Arrhenius rate parameters can be determined:

Equation 9
$$K_{eq}^{i} = \frac{k_{ads}}{k_{des}} = \frac{A_{ads}}{A_{des}} e^{\left(E_{A,des} - E_{A,ads}\right)/RT}$$

Following tests of TBM and water vapor adsorption to bare steel (uncorroded) at four fixed temperatures, a similar methodology to the 1-step mechanism was used. Knowing odorant and water vapor loss over time with Equations 7-9, k_{ads} and k_{des} were derived for TBM and water vapor for each static temperature test. Plotting the logarithmic consumption rate vs. 1/T yields A and E_A for desorption and adsorption of each specie.

Translating these results to the TBM in rusted steel case, yielding Arrhenius rate parameters for each of the four steps outlined above, the following assumptions are made:

- Assume TBM desorption rates are equal to DTBD desorption rates
- All desorption/adsorption rates are treated as equal for steel pipes, corroded or otherwise
- All reactions are first order for gaseous & adsorbed species
- Assume active/inactive sites are not rate limiting and are zeroth order

With these assumptions, we have Arrhenius rate parameters for reaction steps 1, 3, and 4, each involving adsorption and desorption. To calculate the rate parameters for reaction step 2, the one chemical reaction modeled, data from a TBM-rusted steel test from which the overall 1-step Arrhenius rate parameters are known was used. Equations 10 and 11 below represent the rate of destruction/creation of TBM, both as a gaseous and adsorbed specie respectively as steps 1 and 2 in the 4-step mechanism. Similarly, Equation 12 represents the 1-step overall mechanism. Assuming steady state conditions (dX/dt = 0), through substitution k_2 can be estimated with the other rate parameters and known gaseous concentrations of TBM, for a given temperature. With data for two temperatures for k_4, Equation 13 is used to estimate the Arrhenius rate parameters for this reaction step.

Equation 10
$$\frac{d\left[TBM_{(g)}\right]}{dt} = k_{1,des}\left[TBM_{(s)}\right] - k_{1,ads}\left[TBM_{(g)}\right]$$

Equation 11
$$\frac{d\left[TBM_{(s)}\right]}{dt} = k_{1,ads}\left[TBM_{(g)}\right] - k_{1,des}\left[TBM_{(s)}\right] - k_2\left[TBM_{(s)}\right]$$

Equation 12

$$\frac{d\left[TBM_{(g)}\right]}{dt} = -k_{overall}\left[TBM_{(g)}\right]$$

Equation 13

$$\ln\left(\frac{k_{2,@T_1}}{k_{2,@T_2}}\right) = \frac{E_A}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right);\ k_{2@T_1} = Ae^{E_A/RT_1}$$

Experimental Methodology

1) For a non-corroded pipe vessel with a known internal surface area, estimate the site surface density. For example, if a galvanized pipe internal surface is known to be 175 g/m^2, one may estimate that there are 2.68 mol/m^2 active sites. This sets S_o.
2) For a fixed temperature, fill the evacuated vessel with a known quantity of TBM and H_2O (with methane balance). Allow the vessel to come to equilibrium, measure the resulting equilibrium concentrations of TBM and H_2O.
3) Assuming the difference from starting to equilibrium concentrations represent adsorbed species, calculate θ for TBM and water vapor.
4) With values for θ and average background values for partial pressures of species, estimate K_{eq} for TBM and water vapor.
5) One finds for each specie with K_{eq} that there is one equation and four unknowns, two activation energies and two pre-exponential constants. Repeat steps 1-4 for three additional fixed temperatures and solve for these Arrhenius parameters with a system of four equations and four unknowns.

Geometry

The domain of the pipe is modeled as follows:

Pipe Length: The pipe is one foot long.

Pipe Diameter: 2" diameter.

Coverage of Rust for Steel Pipe Data Set: Initially, the entire inner wall will be assumed to have coverage.

Boundary Conditions

The pipe is modeled as a no flow condition (lock-in) with pressure at 60 psi and temperatures of 277°K (4°C or 40°F), 295°K (22°C or 72°F), 313°K (40°C or 104°F), and 333°K (60°C or 140°F). The gas mixture will start with the following volumetric constituents:

TBM cases:
0 ppm di-t-butyl disulfide
1.75 ppm t-butyl mercaptan
Balance = Methane

THT cases:
3.7 ppm THT
Balance = Methane

The pipe outlet is modeled as a passive boundary with no constraints. The pipe wall will be modeled as follows:

Material: steel cases: rusted iron (thermal properties from iron pipe), plastic cases: MDPE (thermophysical properties of MDPE).

Roughness Height: 0.015”

Surface Washcoat Factor: 1.0 (this is a multiplier to the surface area)

New Rate Parameter Results

The third modeling effort also used GTI lab generated data using 2" ID, 1' long pipe segments; steel pipe for TBM loss and MDPE plastic pipe for TBM and THT loss. Both Dataset #1 and Dataset #2 were examined.

The prior analysis of Dataset #1 required the use of a pre-exponential temperature constant (*b*). This parameter, and the new Arrhenius rate parameters and consumption rate results, have been adjusted to reflect true surface reaction rates, as opposed to the previous practice of using volumetric reaction rates, and the assumption of zeroth versus first order rate reactions. Concerning the latter, this is in large part responsible for the significant change in the pre-exponential constant A as derived from Dataset #1.

The parameters shown in the following tables are for zeroth order reactions in that the Arrhenius rate constant is equal to the reaction rate for a given temperature. For one-step reaction mechanisms, this is assumed to be a reasonable approximation, that the global adsorption-reaction-desorption mechanism rate is not dependent on the local odorant concentration.

As the reaction rate parameters are derived from a more robust dataset in the case of Dataset #2, with two additional static temperature test points, the need for the adjustment through the temperature exponent *b* for the new dataset was not anticipated.

Complete results for the two new MDPE pipe tests (Dataset #2) are shown in Table 65. The plots of the Arrhenius rate law in plastic pipe are shown in Figure 69 and Figure 70 for TBM and THT, respectively.

Table 65. Summary of GTI Test Results – TBM/THT MDPE Pipe – Data Set #2

Specie	Temperature (°K)	Steady State Consumption (kgmol/m^2 s)	Calculated Arrhenius Rate Parameters	
			E_A (J/kgmol)	A (kgmol/m^2·s)
TBM	277	3.98839E-16	2.384E+07	1.147E-11
	295	5.11611E-16		
	313	1.67086E-15		
	333	1.85848E-15		
THT	277	5.65500E-15	1.524E+07	5.376E-12
	295	1.47755E-14		
	313	1.74919E-14		
	333	1.79027E-14		

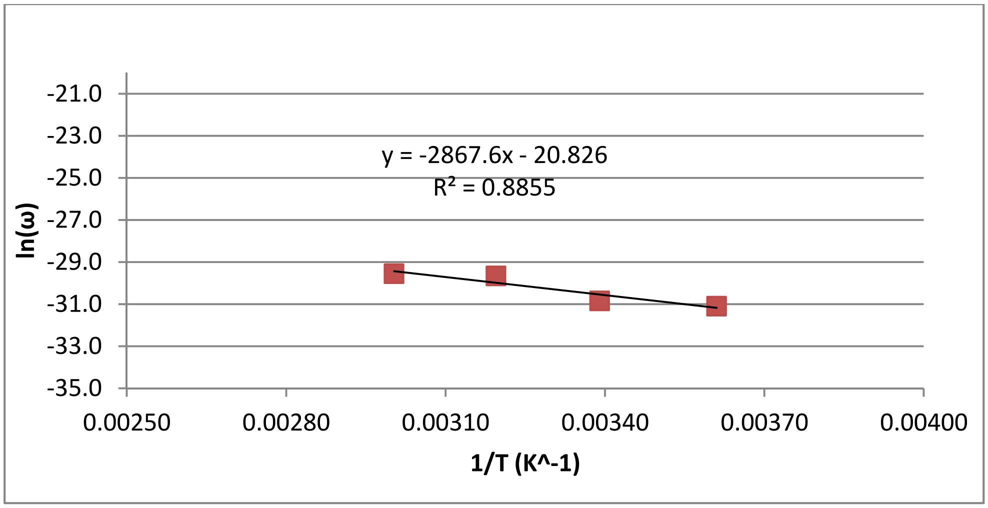

Figure 69. Arrhenius Plot of Data from TBM Loss (Plastic Pipe) – GTI Data Set #2

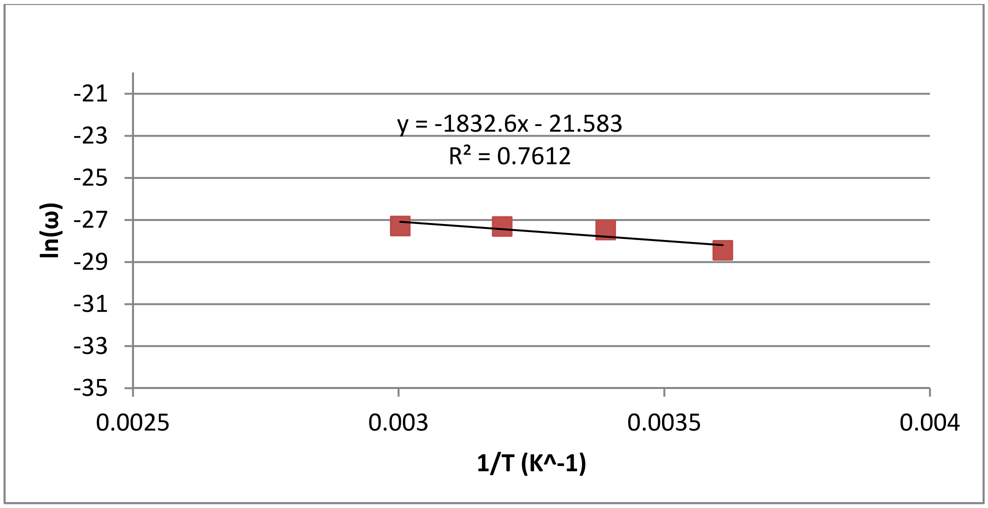

Figure 70. Arrhenius Plot of Data from THT Loss (Plastic Pipe) – GTI Data Set #2

Using test data for TBM loss in bare steel pipe in the presence of a known quantity of water vapor, where net adsorption is also tracked, the adsorption and desorption rate constants can be calculated for the transient and steady state case, shown in Table 66. Using the previously described methodology, these rate constants are ultimately used to generate Arrhenius rate parameters for three of the four reactions within the 4-step mechanism. The quantity of available sites, S_o, was sampled from the measured site density of 7 g/m^2, which results in 0.0061 mol active sites.

Note that per the methodology outlined previously, this multi-step mechanism cannot be modeled as zeroth order, but rather is modeled as a series of first order reactions. Now that the active and inactive sites are explicitly tracked, the reaction rate must be a function of the availability of active surface sites.

The plot of the Arrhenius rate law is shown in Figure 71.

Table 66. Summary of GTI Test Results – TBM Steel Pipe (Uncorroded) – Data Set #2

Temperature (K)	Desorption/Adsorption Rate Constants ($1/m^2 \cdot s$)				Equilibrium Constants	
	$k_{des,TBM}$	k_{des,H_2O}	$k_{ads,TBM}$	k_{ads,H_2O}	$K_{eq,TBM}$	K_{eq,H_2O}
277	6.45E-08	2.33E-04	1.26E-05	1.37E-03	195.09	5.87
295	3.16E-07	2.35E-03	2.50E-05	4.32E-03	79.09	1.83
313	2.62E-06	9.44E-03	1.95E-04	3.05E-02	74.54	3.23
333	1.91E-06	6.89E-03	4.58E-05	1.24E-02	23.96	1.80

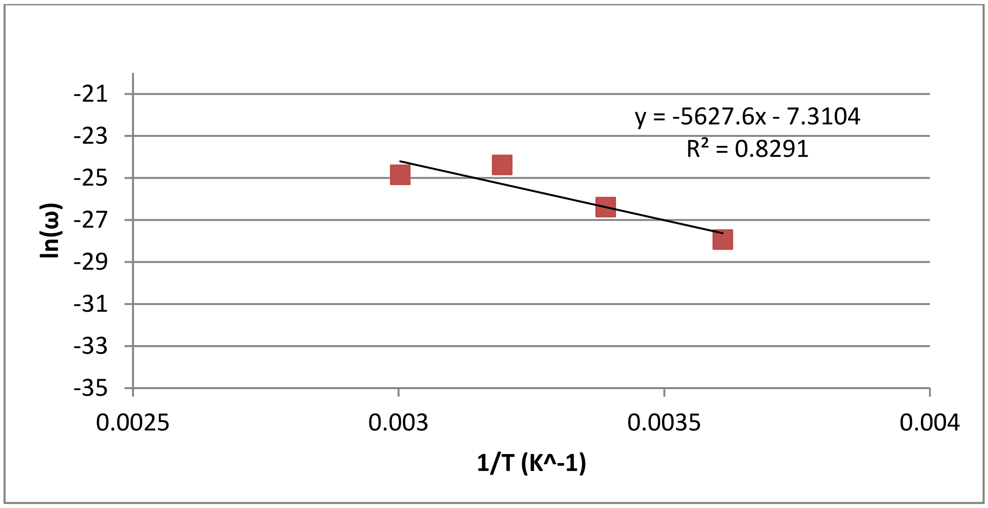

Figure 71. Arrhenius Plot of Data from TBM Loss (Steel Pipe) – GTI Data Set #2

With assumptions outlined in the methodology, the results in Table 66 are translated to the 4-step mechanism when plotted on a logarithmic chart. To estimate the rate parameters for the reaction step, step 2, since the TBM/H_2O data are with bare pipe, the data from Table 66 are compared to data use to generate the original TBM – Steel rate parameters in Dataset #1 to calculate the overall reaction constant $k_{overall}$[4]. The calculated Arrhenius rate parameters are shown in Table 67, which indicate that overall the adsorption and desorption reactions have larger rates than the reaction itself (step 2) and adsorption is favored over desorption for the temperature range considered.

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[4] Note that for units consistency the temperature exponent *b* is neglected.

Table 67. Calculated Arrhenius Rate Parameters for TBM Steel (Corroded) for 4-Step Mechanism

Reaction		Calculated Arrhenius Rate Parameters	
		E_A (J/kgmol)	A (1/m^2·s)
1	Desorption, reverse	5.101E+07	3.495E+02
	Adsorption, forward	2.483E+07	7.788E-01
2	Reaction, forward	5.483E+07	8.943E-04
3	Desorption, forward	5.101E+07	3.495E+02
4	Desorption, reverse	4.830E+07	5.171E+05
	Adsorption, forward	3.576E+07	1.002E+04

Modeling Results from Data Set #1

Modeling was also performed for the new rate parameters as calculated from the old GTI data, summarized in Table 68. As mentioned before, an important aspect of this revised modeling is the shift from the use of a thin volumetric reaction zone to surface chemistry on the interior wall itself, requiring a shift in both how parameters are treated and which submodels are deployed. For the new rate parameters, the following figures (Figure 72 through Figure 75) show model results as compared to test data. Data are shown without scaling to highlight that despite the increase in accuracy, the transient models are based upon long term, near steady state results to determine the reaction rate parameters. Agreement is determined by relative comparison of the linear fit of experimental data to the model data.

Table 68. Summary of Prior GTI Test Results, Revised for New Model

Specie	Pipe Mat'l	Temperature (K)	Steady State Consumption (kgmol/m^2·s)	Calculated Arrhenius Rate Parameters		
				E_A (J/kgmol)	A (kgmol/m^2·s·T^b)	b
TBM	MDPE	274	4.15440E-16	2.509E+07	2.525E-11	0.5
		294	8.78872E-16			
	Steel	274	2.50799E-19	5.065E+07	1.135E-09	1.7
		294	1.13807E-18			
THT	MDPE	274	5.55799E-18	4.379E+07	1.243E-09	1.0
		294	2.05540E-17			
	Steel	274	1.70380E-18	2.823E+07	4.111E-13	1.5
		294	3.95896E-18			

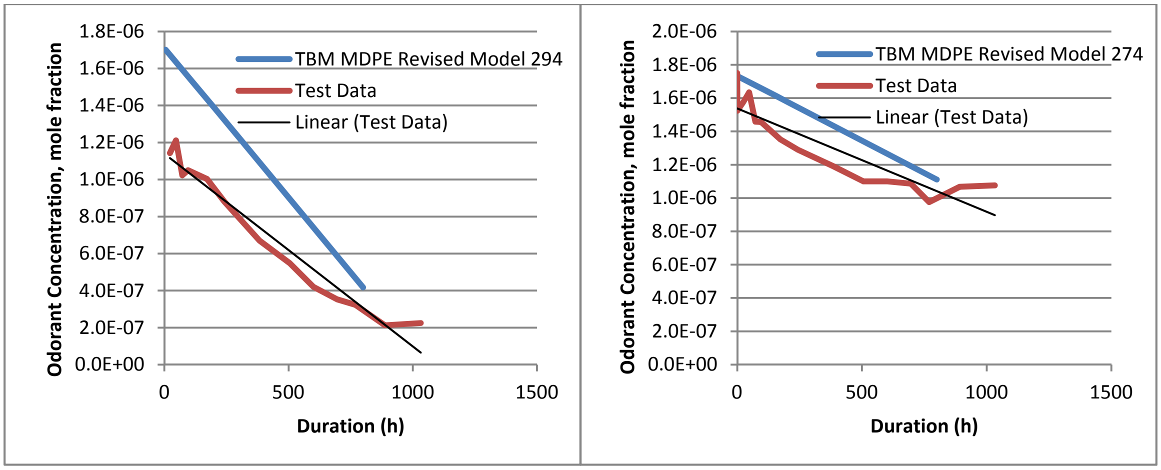

Figure 72. Data and Model Results for Revised Data – TBM in MDPE Pipe

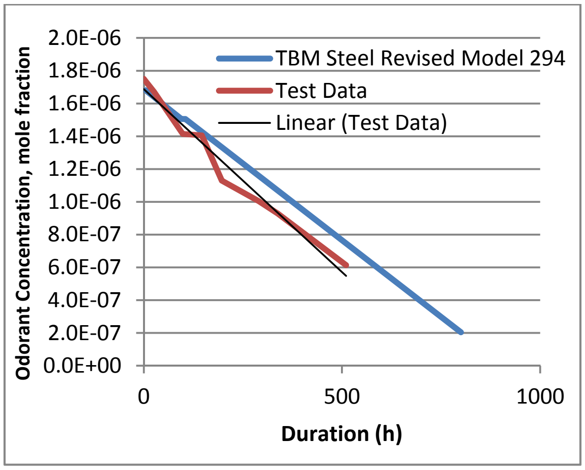

Figure 73. Data and Model Results for Revised Data – TBM in Steel Pipe[5]

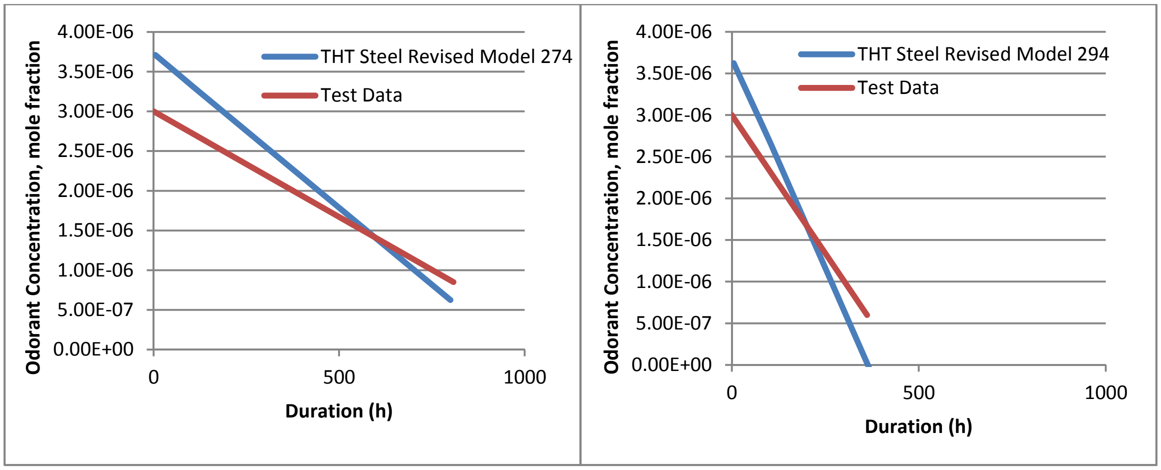

Figure 74. Data and Model Results for Revised Data – THT in Steel Pipe[6]

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[5] Data from 274 K testing was found to be faulty and not used for validation

[6] Two test data points recorded only, *b* selected to slightly overestimate odor fade due to typical shape of test data curve

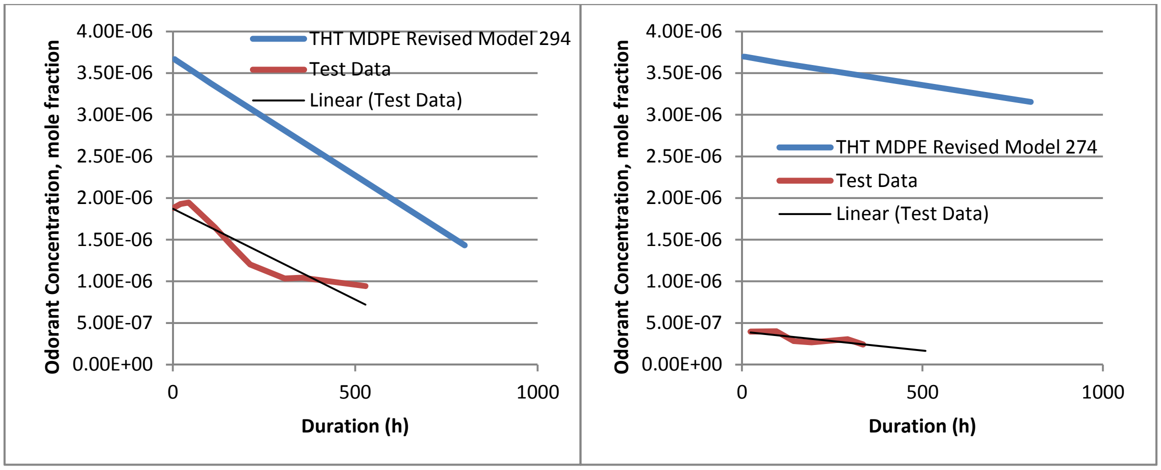

Figure 75. Data and Model Results for Revised Data – THT in MDPE Pipe

Modeling Results from Data Set #2

In Figure 76 and Figure 77, the benefit of developing the reaction rate using multiple temperature rating points, four instead of two, is shown where good agreement is reached with the data without the use of a temperature exponent *b*, which is in effect an empirical fitting constant. For both MDPE pipe cases, THT and TBM, the parameters in Table 65 work well.

Overall, for prior GTI tests at two temperatures and more recent tests at four temperatures, experimental test results consistently show a strong initial drop in odorant concentration as active surface sites are occupied, a dynamic aspect of testing that is not compatible with the Arrhenius model overall without state-dependent constants (i.e. *A* is a function of odorant concentration). However, this does correlate with experiences on newly installed pipe, a situation where odorant and other species are not initially occupying any available surface sites. One may use the parameters in Table 65 and Table 66 to generate order of magnitude predictions.

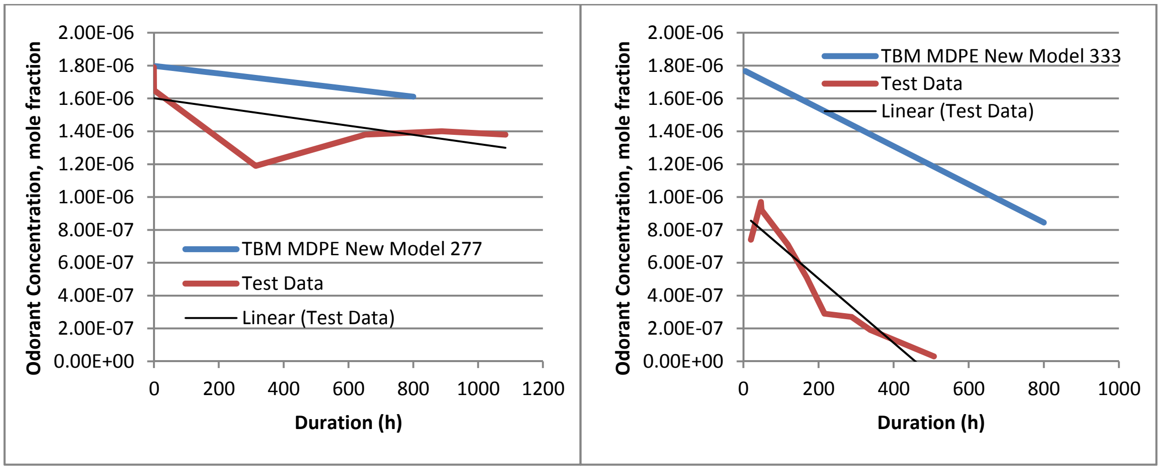

Figure 76. Data and Model Results for New Data – TBM in MDPE Pipe

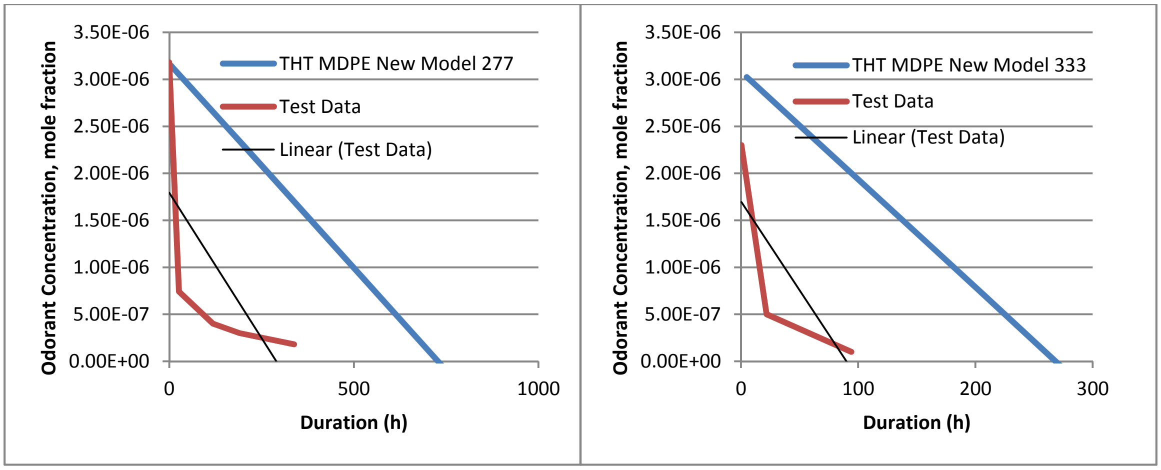

Figure 77. Data and Model Results for New Data – THT in MDPE Pipe

Concerning the new TBM odor fade in steel pipe data, where a more complex reaction mechanism has been developed (shown in Table 67), the results comparing the 1-step mechanism (which glosses over the influence of water vapor) gives decent agreement with the high temperature case (333 K) but exhibits poor agreement with the low temperature case (277 K). See Figure 78.

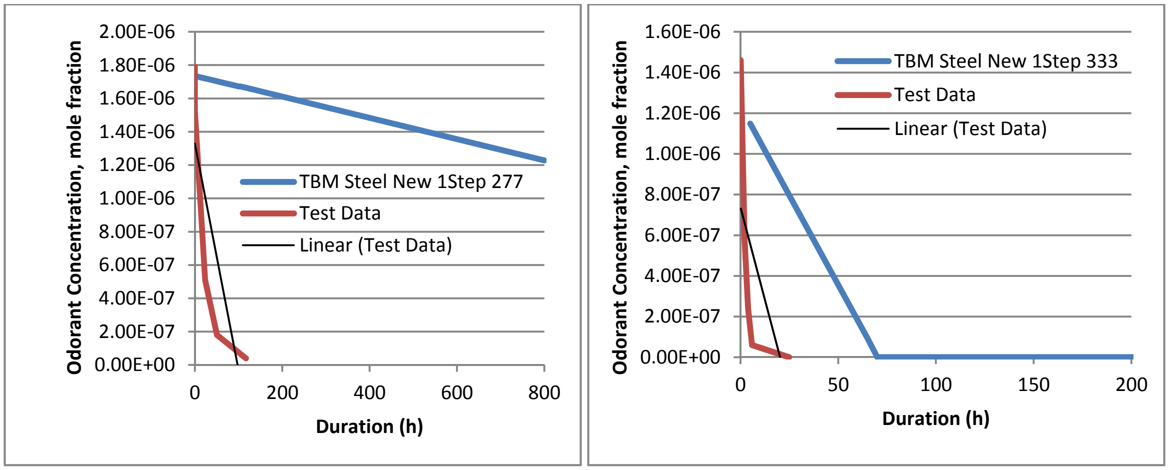

Figure 78. Data and Model Results for New Data – TBM in Steel Pipe with 1-Step Version

When the multi-step reaction rate mechanism is modeled as a 6-step mechanism, with the forwards and backwards rates of reactions 1 and 4 in Table 67 treated separately, the multi-step mechanism shows better agreement but still shows a more aggressive treatment of the initial adsorption step as shown in Figure 79. The sharp drop-off in TBM via adsorption is overestimated by the model which, if predictions were necessary on the order of a day or two the error would be significant, but for multiple days the multi-step model shows much better agreement than the 1-step mechanism for the observed overall drop-off from the recent GTI dataset.

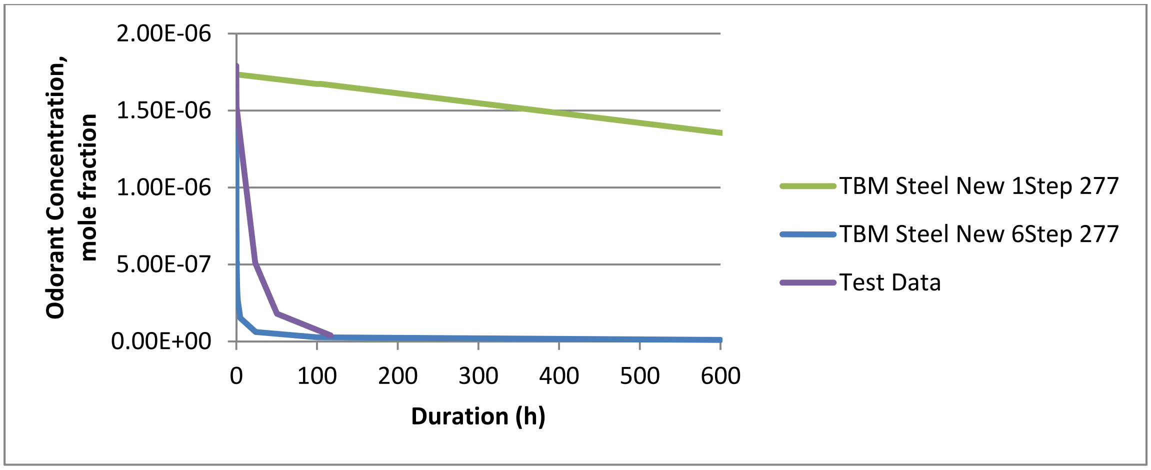

Figure 79. Data and Model Results for New Data – TBM in Steel Pipe with 1 & 6-Step Version

Conclusions

In this update to prior odor fade modeling, the complete reaction rate mechanisms are described for multiple 1-step reactions with adjustments necessary for surface versus volumetric reactions, for TBM and THT fade in both steel and MDPE pipe, as derived from GTI datasets. Overall, these 1-step parameters generally yield modeling results with good agreement to the test data for the range of temperatures tested. Additionally for TBM in rusted steel pipe, which fades as a multi-step process, a methodology was created to derive the reaction rate parameters for the various desorption, adsorption, and reaction steps. Initial modeling of the 1-step versus multi-step reaction mechanism showed the multi-step mechanism to be more robust and accurate as a predictive model.

Despite the limited agreement shown for this multi-step reaction mechanism, more datasets are needed under controlled conditions to better calibrate the multi-step rate parameters with steel pipe, specifically the tracking of multiple species with rusted pipe. This recommended testing is outlined in the Recommendations for Future Testing section.

Tests on Flowing Gas Loop

A 20-foot long 2-inch MDPE test loop was constructed to perform some limited testing on flowing gas containing TBM. The loop contained three sampling points attached with heat fused saddle tees as shown in Figure 80.

Figure 80. Flowing Pipe Loop

Two tests were performed. In Test A, flowing house gas was used. In Test B, flowing gas from a nominal 2 ppmv TBM in methane gas was used. Experimental parameters are listed in Table 69. For both cases, the gas was sampled at three points during a one-day test period after which the gas was locked in and resampled the next day.

Table 69. Flowing Loop Data

Test	Gas and Odorant	Pressure	Flow	Temperature
A	House Gas, TBM and DMS	8" w.c.	1.3 ft^3/hr	72°F
B	TBM in Methane	60 psig	1.5 Liter/min	72°F

The results for Test A are shown in Table 70. This experiment was meant to simulate what happened in a newly installed residential or commercial building past the meter when plastic piping was used. No odor fade was noted over the course of the day, but when the gas was tested on the following day, after it was locked in, a 6% loss in the TBM data was found. Also present in the gas were H_2S and DMS, both of which experienced loss at 25% and 17% respectively. This experimental data bears out what was observed in lab experiments, in that TBM does absorb into the plastic material.

Another test was performed at a higher pressure (Table 71). This time, no odor loss was measured. The initial low value at the first sampling period for test points 1 and 2 are due to mixing issues as these are the first two points downstream of where the gas was introduced.

The data for this test is inconclusive but may indicate as long as gas is flowing at the higher pressure, no odorant loss would be expected.

Table 70. Flowing Test Loop Results for Test A

Test	Test Point	Hours	ppmv TBM	ppmv DMS	ppmv H_2S
A	1	1.00	2.38	1.31	1.77
		3.03	2.38	1.27	1.84
		4.95	2.37	1.27	1.77
		7.08	2.45	1.31	1.7
	2	1.13	2.36	1.27	1.76
		3.12	2.33	1.24	1.79
		5.02	2.41	1.29	1.82
		7.15	2.44	1.29	1.7
	3	1.23	2.43	1.29	1.7
		3.18	2.35	1.23	1.77
		5.17	2.35	1.26	1.83
		7.23	2.49	1.28	1.64
	Final	23.73	2.24	1.04	1.30
% Loss from Average Data			6	17	25

Table 71. Flowing Test Loop Results for Test B

Test	Test Point	Hours	ppmv TBM
B	1	0.85	1.33
		2.67	1.73
		4.70	1.79
		6.72	1.76
	2	0.88	1.23
		2.72	1.76
		4.75	1.63
		6.75	1.76
	3	0.97	1.62
		2.77	1.81
		4.80	1.77
		6.82	1.71
	Final	29.83	1.74

Recommendations for Further Work

The modeling data is incomplete due to the lack of field data to confirm and update the draft models. This project used three iterations of laboratory data to generate the initial models.

The first iteration used literature data. Odorant consumption rates based on literature data were less than anticipated. The data was incomplete from the perspective of assessing the pressure-dependency of odorant consumption reactions. In addition, it was skewed in the treatment of second-order temperature effects, in that the odorant consumption had an inverse relation to temperature.

The second iteration used data GTI generated laboratory data. From these additional runs, a high correlation was observed for odorant consumption rates especially when a temperature dependency was included in the Arrhenius rate expression.

However when the models were used to simulate field conditions inconsistencies were noted. From lab data and practical experience, it is known that t-butyl mercaptan (TBM) is more reactive with the steel pipe material than with the plastic pipe material and that TBM will be more reactive than tetrahydrothiophene (THT). In the new models both odorants, especially THT, were being over consumed. Comparison to the limited field data we had confirmed this discrepancy.

This disagreement initiated a rerun of the lab testing at four different temperatures to generate new Arrhenius rate data. This dataset was analyzed using an assumption of zeroth versus first order rate reactions (different from the iteration using the initial GTI data). An important aspect of this revised modeling is the shift from the use of a thin volumetric reaction zone to surface chemistry on the interior wall itself, requiring a shift in both how parameters are treated and which submodels are deployed. In addition, a more complex approach to the decomposition of TBM in the presence of rusted steel was derived and tested.

Despite the limited agreement shown for this multi-step reaction mechanism, more datasets are needed under controlled conditions to better calibrate the multi-step rate parameters after that performed for bare steel pipe, specifically the tracking of multiple species with rusted pipe.

The following lab tests are recommended to resolve the issue:

1) In a new test rig, comprising a corroded pipe vessel with a known internal surface area, estimate the site surface density, again setting S_o.

2) For a fixed temperature corresponding to the initial temperature used in Dataset #2, fill the evacuated vessel with a known quantity of TBM (with inert balance).

3) For testing at this fixed temperature, monitor the concentrations of TBM(g), H_2O(g), and DTBD(g) over time.

4) Repeat for the same three additional temperatures from Dataset #2. Use the resulting concentrations in the methodology outlined below to estimate the reaction rate of step 2 in Table 67 (forward reaction of TBM with active iron sites to generate di-t-butyl disulfide.

5) Analytically, this yields 6 equations and 6 unknowns, below this is shown where the unknowns are in **bold**:

    I. **Rate_1 (at T_1)** = k_1*[TBM(g)]
    II. **Rate_2 (at T_1)** = **k_2*[TBM(s)]**
    III. Rate_3 (at T_1) = k_3***[DTBD(s)]**
    IV. Rate_4 (at T_1) = k_4***[H_2O(s)]**
    V. **[TBM(s)]** = **Rate_1 (at T_1)***time – **[DTBD(s)]**
    VI. **[H_2O(s)]** = **Rate_2 (at T_1)***time – [H_2O(g)]

6) With k_2 known and using the assumptions outlined in the Methodology section of this document, estimate the Arrhenius parameters E_A and A by repeating these steps for a second temperature, T_2 and using the Equation 8, verifying for additional temperatures.

Additionally, the same testing in steel pipe should be performed with THT. It is anticipated that THT would be much more stable, hence it was not prioritized during this first phase.

And finally, as the project progressed, it unfortunately became clear that economic factors delayed many significant new construction projects for the stakeholders contacted. This lack of construction projects made it difficult to obtain field test data from companies otherwise willing to participate. The lack of field data made it impossible to make improvements to the various iterations of the model.

Some limited testing was done on flowing gas in plastic pipe, but time and funding constraints prevented testing in steel pipe.

To summarize, the following are recommendations for additional testing.

- Perform additional lock-in testing on rusted steel pipe with TBM and water to more fully develop the current model.
- Perform the same testing on THT in bare and rusty steel pipe.
- Construct a flowing steel pipe to simulate additional field test data.
- Continue to solicit for field data from interested parties.

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List of Acronyms

Acronym	Description
AGA	American Gas Association
BTEX	Benzene, Toluene, Ethyl benzene, Xylenes
CPSC	Consumers Product Safety Commission
DMS	Dimethyl Sulfide
DOT	Department of Transportation
DTBDS	Di-tertiary-butyl Disulfide
EM	Ethyl Mercaptan
EIA	Energy Information Administration
GC	Gas Chromatography
GTI	Gas Technology Institute
IGT	Institute of Gas Technology
IPM	Isopropyl Mercaptan
LDC	Local Distribution Company
LP	Liquified Petroleum
LPG	Liquified Petroleum Gas
MEA	Monoethanol Amine
MES	Methyl Ethyl Sulfide
MM	Methyl Mercaptan
MMSCF	Million Standard Cubic Feet
NFPA	National Fire Protection Association
NIST	National Institute of Standards and Technology
NPGA	National Propane Gas Association
NPM	Normal Propyl Mercaptan
NPS	Nominal Pipe Size
PE	Polyethylene
PHMSA	Pipeline and Hazardous Materials Safety Administration
PVC	Polyvinyl Chloride
TBM	Tertiary Butyl Mercaptan
THT	Thiophane or Tetrahydrothiophene

END OF REPORT