the Energy to Lead

Odorant Effectiveness

DOT/PHMSA Webinar to Disseminate Project Results

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gti

GTI at a Glance…

- Not-for-profit research, organization with a 70 year history
- Facilities
  - 18 acre campus near Chicago
  - 200,000 ft^2, 28 specialized labs
  - Other sites in DC, CA, MA, PA, and Alabama
- Staff of 250
  - 170 scientists, engineers, and technicians, covering many different disciplines

Offices & Labs

Flex-Fuel Test Facility

Energy & Environmental Technology Center

Project Sponsors

> DOT/PHMSA

- DOT Project # 363
- Contract Number: DTPH56-10-T-000018

> Consortium of LDCs

- OTD Project 7.10.b

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Agenda

- Background
- What is odor fade?
- Why is it significant?
- What are the types of odorant interaction?
- Most recent results from the odorant effectiveness project
- Project challenges

Background - Past IGT/GTI Odor Fade Research

- March 1962 to study the kinetics of various reactions leading to odor fading.
- 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.
- Some initial equations were generated.
- Project terminated in 1965.

Odor Fade vs Odor Masking

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

Odor Fade – Not a New Problem

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

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

Typical Odorant Interactions – Adsorption

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

Adsorption versus Absorption

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Typical Odorant Interactions – Absorption

- **Absorption** is the filling of pores in a solid, or dissolution into a liquid.
- The substance being absorbed is physically taken up by the bulk material and is partitioned between the gaseous phase and the solid or liquid phase.
- Not only can odorants be physically absorbed into plastic 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.

Typical Odorant Interactions – Oxidation

Oxidation is when the odorant chemically reacts with rust present on steel pipe, although any oxidizing compound promotes the reaction.

> The rust derives from the process used to manufacture pipe for the natural gas industry.

- All hot-rolled steel products contain mill scale on the outer surfaces.
- Bluish black form of iron oxide commonly called magnetite (Fe_3O_4) and contains iron in both the +2 and +3 valence state.
- Breaks in the mill scale allow rusting to occur.
- Rust consists of hydrated iron(III) oxide ($Fe_2O_3 \cdot nH2O$) and iron(III) oxide-hydroxide ((FeO(OH) and $Fe(OH)_3$), all having a characteristic reddish orange color.

Typical Odorant Interactions – Oxidation

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

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

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

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

Overcoming 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.
- Decisions vary from company to company and are often anecdotal at best.

Objectives of GTI Project

- In 2010 GTI initiated an industry collaborative project to research, model, and validate issues associated with natural gas odorant fade.
- DOT/PHMSA provided funding in a related project later that year.
- The goal of the combined project was to develop a model to describe odor fade in gas pipelines.
- The ultimate goal was to provide a "Practical Pipeline Operator Guide" to manage odor fade issues associated with typical gas system operating conditions and materials of construction.

Tasks of GTI Project

1. Review odor fade information from industry sources, standard documents, research reports, and publications in scientific journals to identify known variables.
2. Reduce the number of initial variables using thermodynamic prescreening and operator experience.
3. Perform chemical stability testing using t-butyl mercaptan (TBM) in inerted reactors.
4. Measure temperature responsiveness to determine the Energy of Activation for the Arrhenius rate equations using TBM and tetrahydrothiophene (THT) in steel and plastic reactors.

Tasks of GTI Project, continued

5. All of this data was collected with the purpose of generating a preliminary odor fade model using ANSYS® Fluent®, a fluid flow simulation software package.
6. Compare lab data with data obtained from the field.

Chemical Stability Testing

- This series of tests were conducted in stainless steel gas sampling cylinders that were inerted with a silicon-containing coating on the interior of the cylinder.
- These containers were designed to be used as “control reactors” for comparison with results obtained with standard industry chemicals.
- TBM used because it has high reactivity.

Parameters Tested

- Data from the control test was statistically compared ($p<0.05$ or 95% confidence limit) to data from tests with added components to gauge the impact on odorant concentration.

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

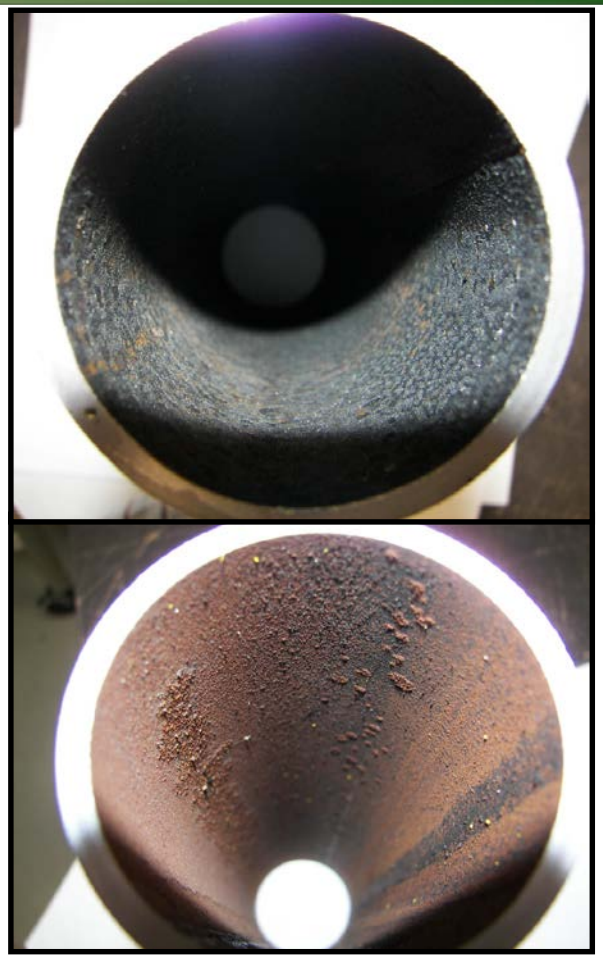
- MEA selected as a surrogate amine compound representing volatile amine compounds used for natural gas treatment and as a constituent in hydraulic fracturing fluids.

Chemical Interaction Results

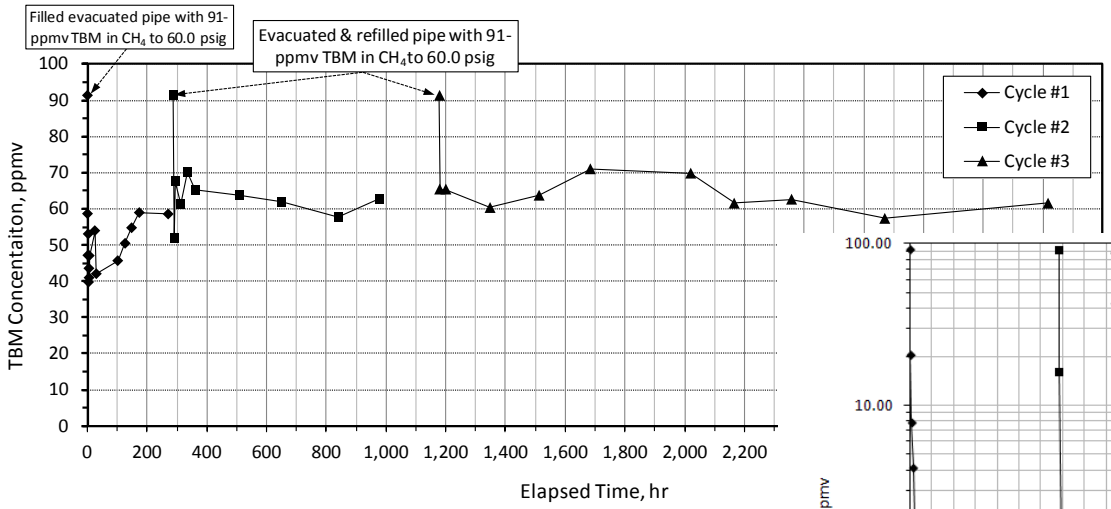
- Results from these experiments showed there was no TBM odorant fading in the presence of
  - Up to 1000 ppmv oxygen,
  - 19 ppmv methanol,
  - 1000 ppmv hexanes,
  - 141 ppmv water.
- There was evidence of odor fade in the presence of
  - 152 ppmv methanol and
  - ~60 and 21 ppmv monoethanolamine (MEA).

Rust in Steel Pipe Results

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

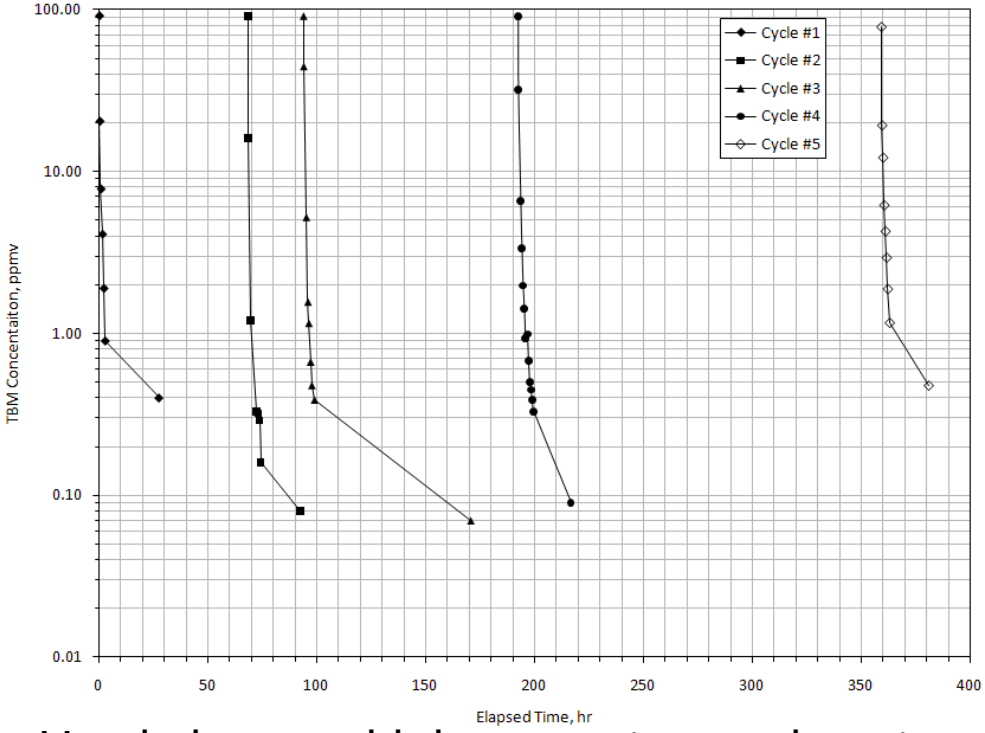


Rust in Steel Pipe Results



Off the shelf pipe - decrease to a steady state condition

Later introduction of lower concentration odorant showed stability. TBM loss rate of only ~0.02 ppm/100 hours



Used pipe - rapid decrease to no odorant

Quenching with Liquid TBM

- Testing with liquid TBM injected to quench a used rusty pipe also showed a rapid loss of TBM.
- The amount of odorant to use was estimated from two different sources.
  1. The first was odorant application rate data used for pipeline conditioning that were available in the literature and from the survey data.
  2. In a private communication with a pipeline company, an odorant application rate of 0.25 ml per ft^2 of internal pipe surface area was reported as being used for their pipeline conditioning. This rate was based on the amount of odorant estimated to be required to create a wall film thickness of 0.254 micron.

Quenching with Liquid TBM

- For the testing at GTI, it was decided to initially use approximately ¼ the amount per injection or cycle (equivalent to 283 ppmv TBM), to prevent over saturation of the inner pipe wall with the TBM and to study the impact of several iterations.
- 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.

Cycle	Initial Rate Loss of TBM, ppmv/hour
1	150
2	137
3	158
4	33
5	19
6	40
7	34

Quenching with Liquid TBM

- This data confirmed field data from four case studies of pre-odorization/pickling.
- 0.2 to 0.4 milliliter per square foot of odorant addition was required to achieve full conditioning.
- The field data also found that nearly double the odorant addition rate was required when using a continuous liquid addition technique, and that the odorant addition rate was significantly lower (0.05 mL/ft^2) 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 seems reasonable.

Modeling Using Lab Data

- Ansys Fluent software was used to create the initial odorant consumption models.

$$k = Ae^{-\frac{E_a}{RT}} \quad or \quad ln\ k = -\frac{E_a}{RT} + ln\ A$$

Where:

k =	Chemical Reaction Rate
A =	Pre-exponential Factor
E_a =	Activation Energy
R =	Gas Constant
T =	Temperature in Kelvin

- It needs inputs regarding properties of the species and reactions that are not always readily available in the literature, specifically the Activation Energy of the reaction.
- This property is defined as the minimum energy necessary for a chemical reaction to occur. It can be experimentally derived, using the Arrhenius equation, from experiments that measure rates of reaction at different temperatures.

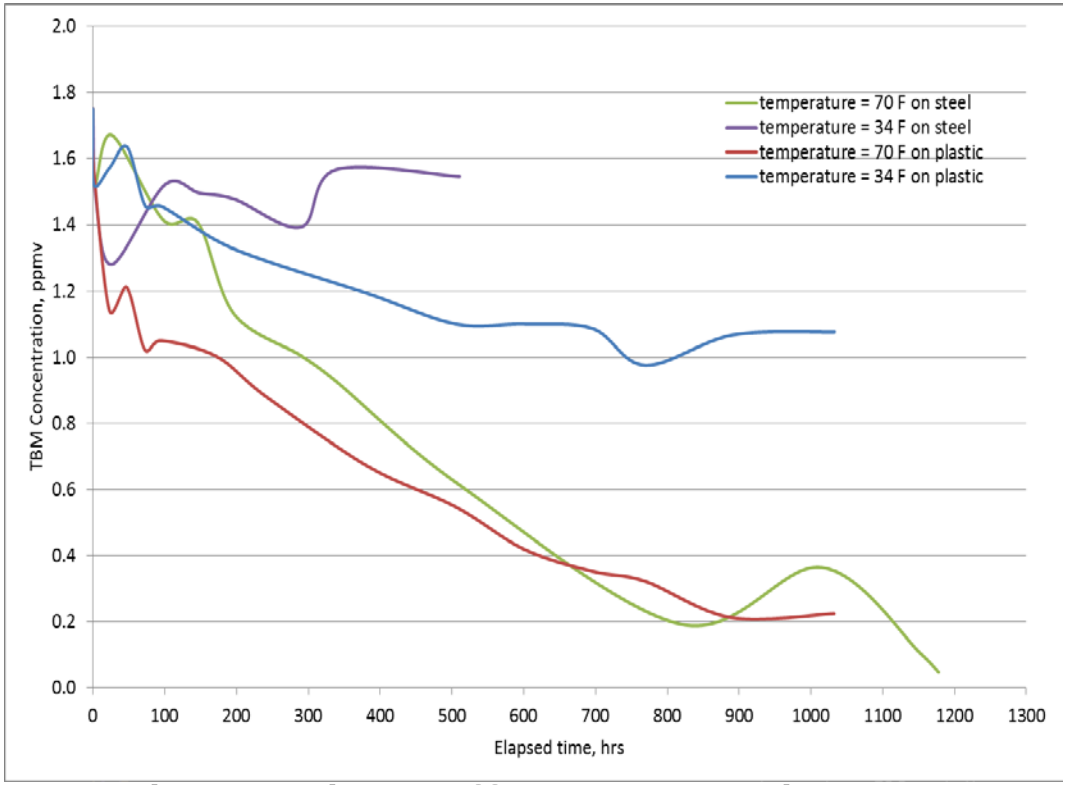
Modeling Using Lab Data

- Four different types of experiments were performed; TBM and THT (separately) in both steel and plastic pipe.
- Lab experiments were setup using these conditions:

Parameter/Variable	Value or Range	Value or Range
Pipe Material	Steel, Plastic	Steel, Plastic
Pipe Length	1.0 ft.	1.0 ft.
Pipe Diameter	2-inch NPS Schedule 40	2-inch NPS Schedule 40
Pipe Corrosion Level (Steel)	As received	As received
Gas Pressure	60 psig	60 psig
Temperature	70°F and 34°F	140°F, 104°F, 72°F and 40°F
TBM	2 ppmv	2 ppmv
THT	4 ppmv	4 ppmv

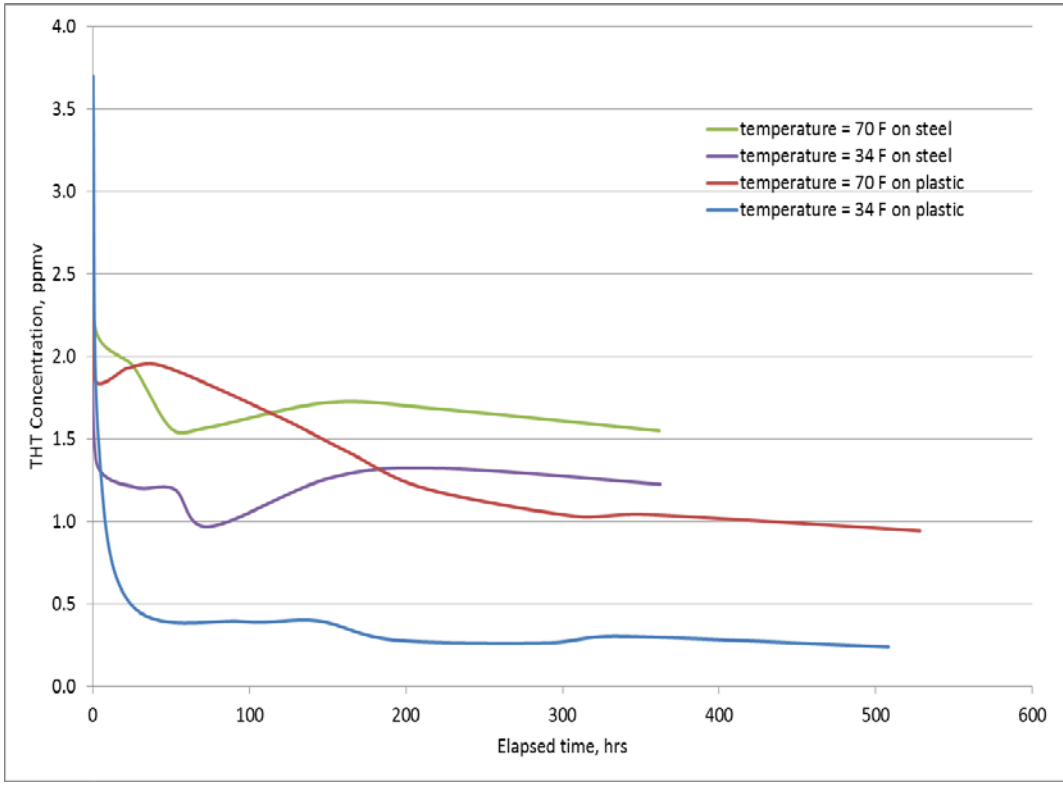
Modeling Using Lab Data – TBM – Steel and Plastic at Two Temps

- TBM was more reactive with the steel pipe material at the higher temp (green) than at the lower temp (purple).
- But loss of TBM is also noted in the plastic pipe at the higher temp (red).
- Loss of odorant in the plastic pipe may indicate an absorption effect occurring where the higher temp promotes absorption of the TBM into the plastic matrix. At a lower temperature the impact is less.



Modeling Using Lab Data - THT– Steel and Plastic at Two Temps

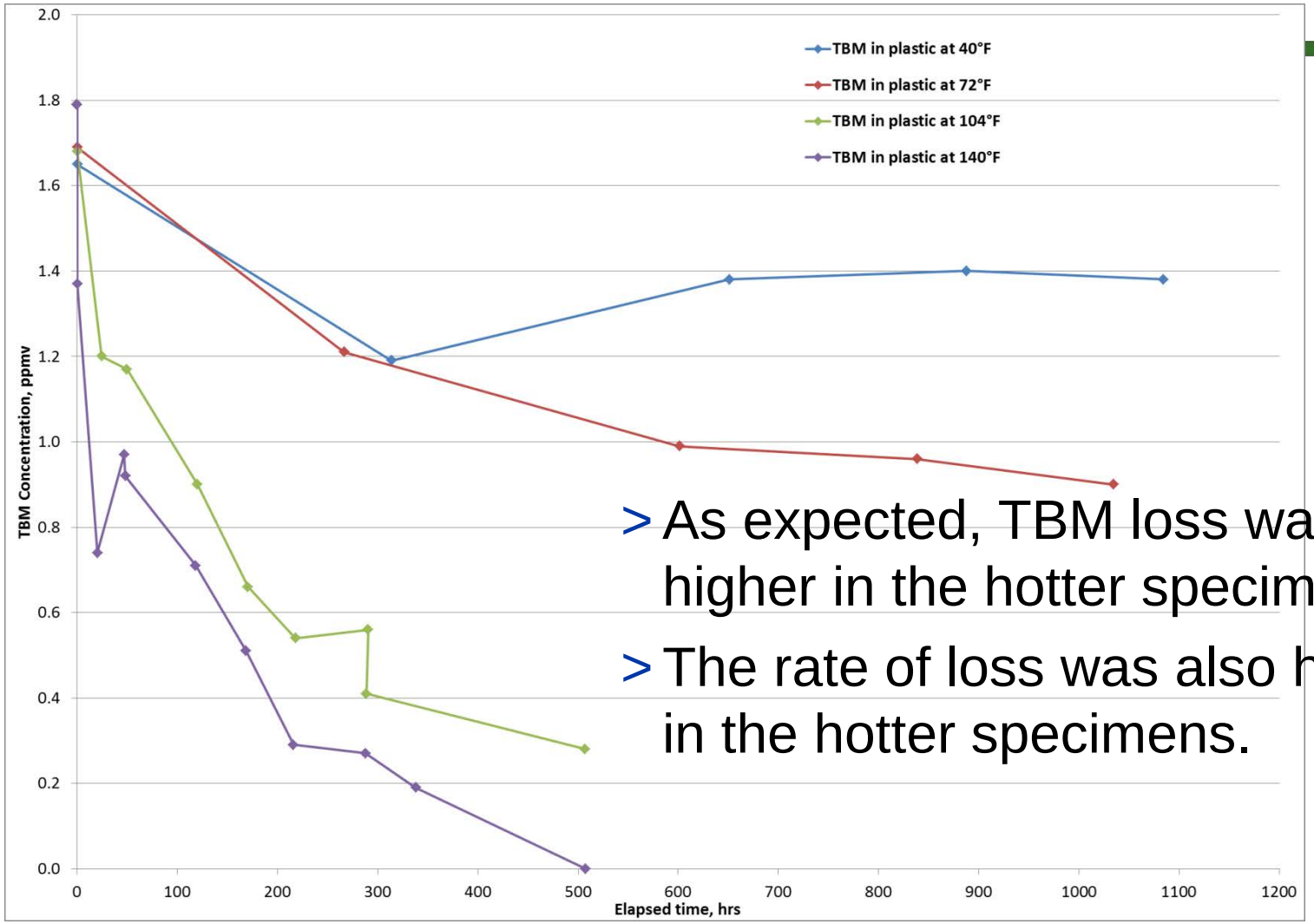
- The opposite phenomenon occurred with THT.
- At the higher temps the overall final odorant losses were less than at the lower temp.
- Could be condensation, but it's not necessarily supported by the literature.



Next Steps

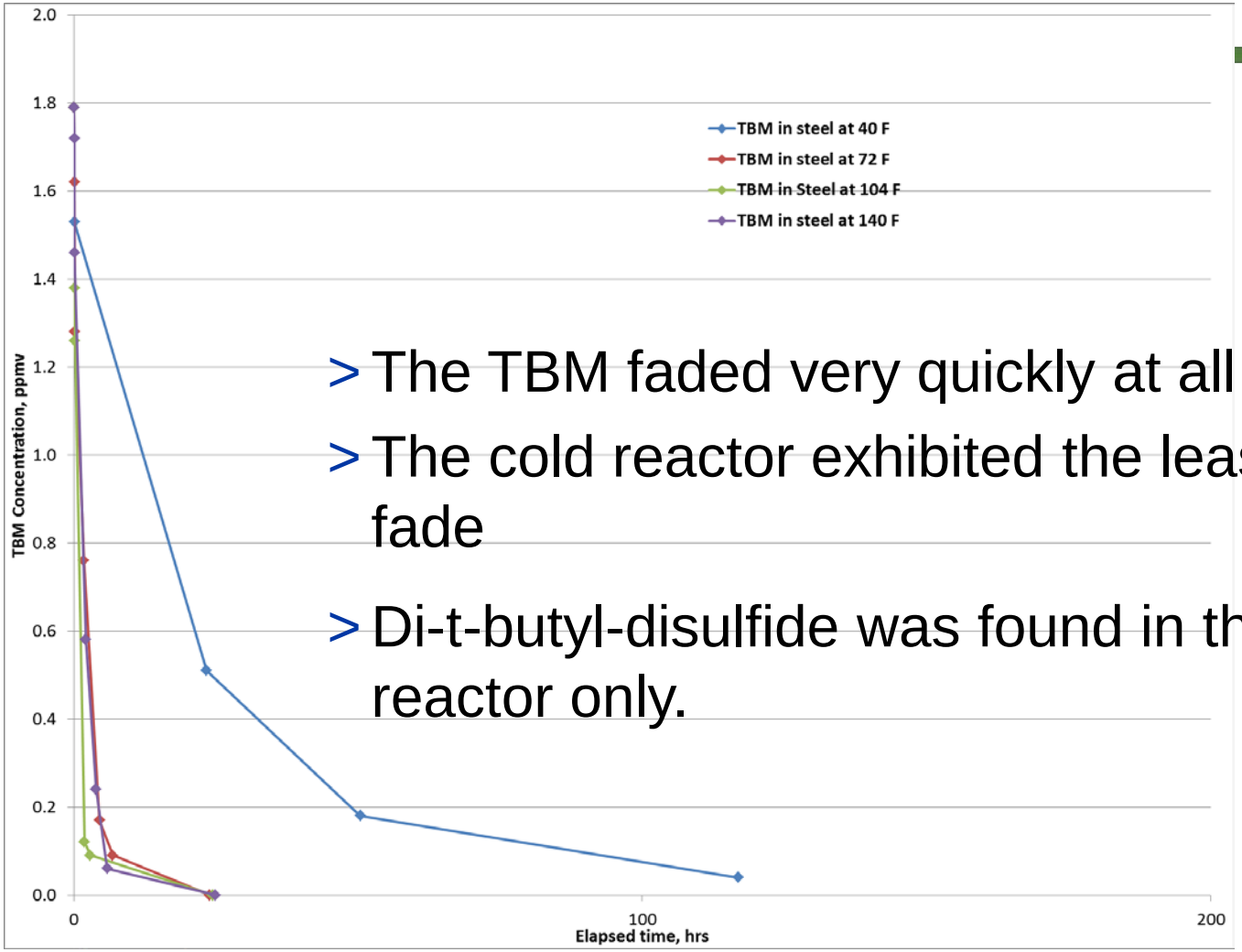
- When the GTI datasets were modeled, a high correlation was observed for odorant consumption rates, especially when a temperature dependency was included in the Arrhenius rate expression.
- However, when the limited field data available was applied, the models were overestimating the odorant loss.
- We performed some additional tests to investigate the phenomena and further expand the data set by studying multiple temperatures and interactions with water.

Modeling Using Lab Data – TBM – Plastic at Four Temperatures



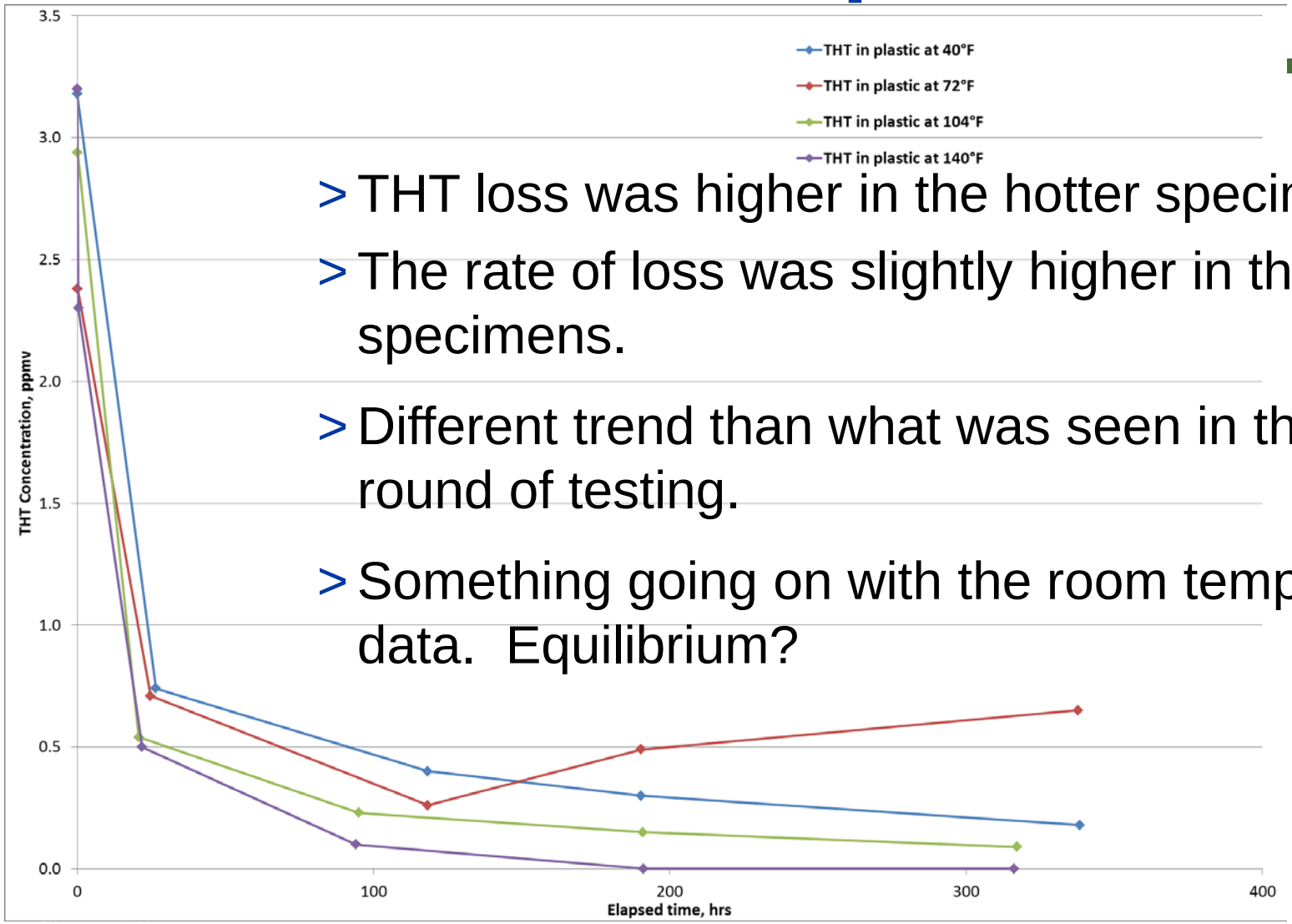
- As expected, TBM loss was higher in the hotter specimens.
- The rate of loss was also higher in the hotter specimens.

Modeling Using Lab Data – TBM – Steel at Four Temperatures with H_2O



- The TBM faded very quickly at all temperatures.
- The cold reactor exhibited the least amount of fade
- Di-t-butyl-disulfide was found in the hottest reactor only.

Modeling Using Lab Data - THT– Plastic at Four Temperatures



- THT loss was higher in the hotter specimens.
- The rate of loss was slightly higher in the hotter specimens.
- Different trend than what was seen in the first round of testing.
- Something going on with the room temp final data. Equilibrium?

Odorant Models

- The first draft model used a parametric analysis to determine the loss of TBM odorant, with a combination of TBM and its dimer decomposition product, di-t-butyl disulfide.
- It was based on literature data.
- When the limited field data available was applied, the models were overestimating the odorant loss.
- In addition, the models were skewed in the treatment of second-order temperature effects, in that the odorant consumption had an inverse relation to temperature.

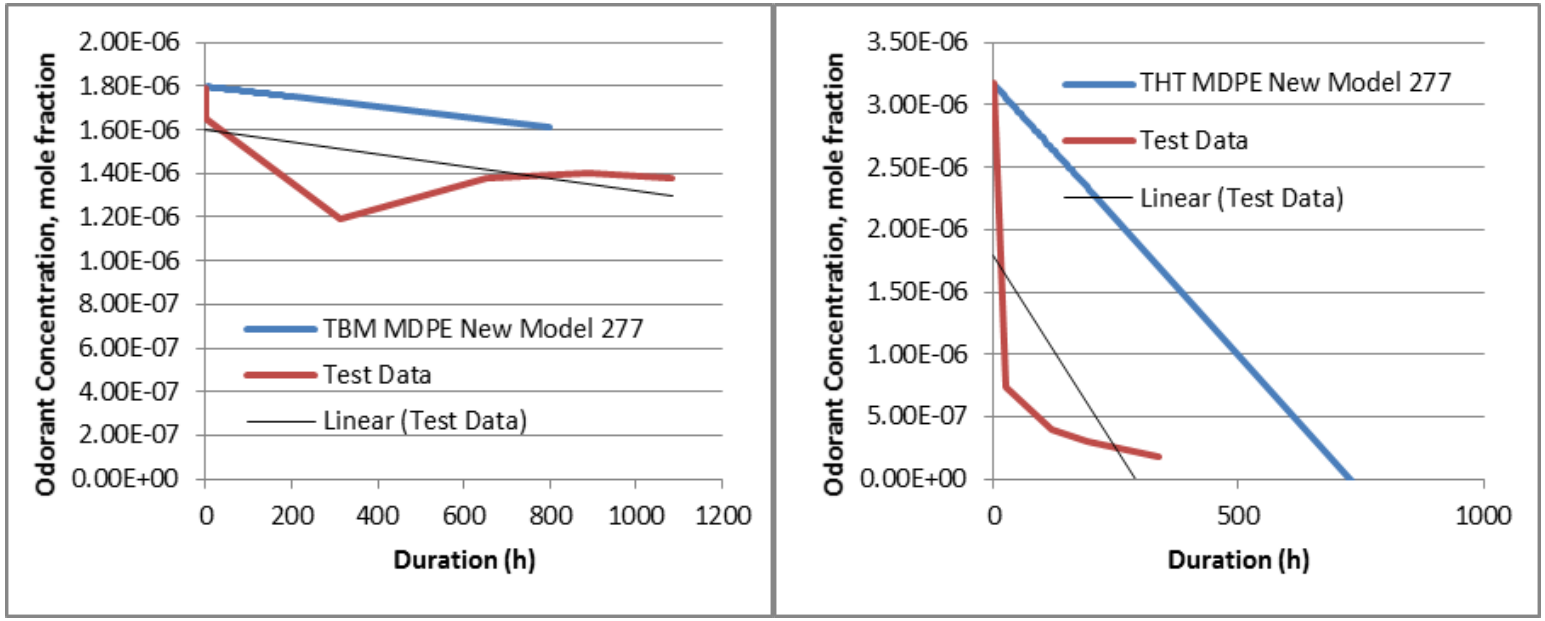
Odorant Models

- The second model used GTI data generated at two different temperatures.
- This dataset was an improvement as it eliminated the inverse temperature effect seen with the literature data.
- Plastic pipe and THT were modeled on an assumption of adsorption and/or absorption.
- However, this model also over estimated odorant loss.

Odorant Models

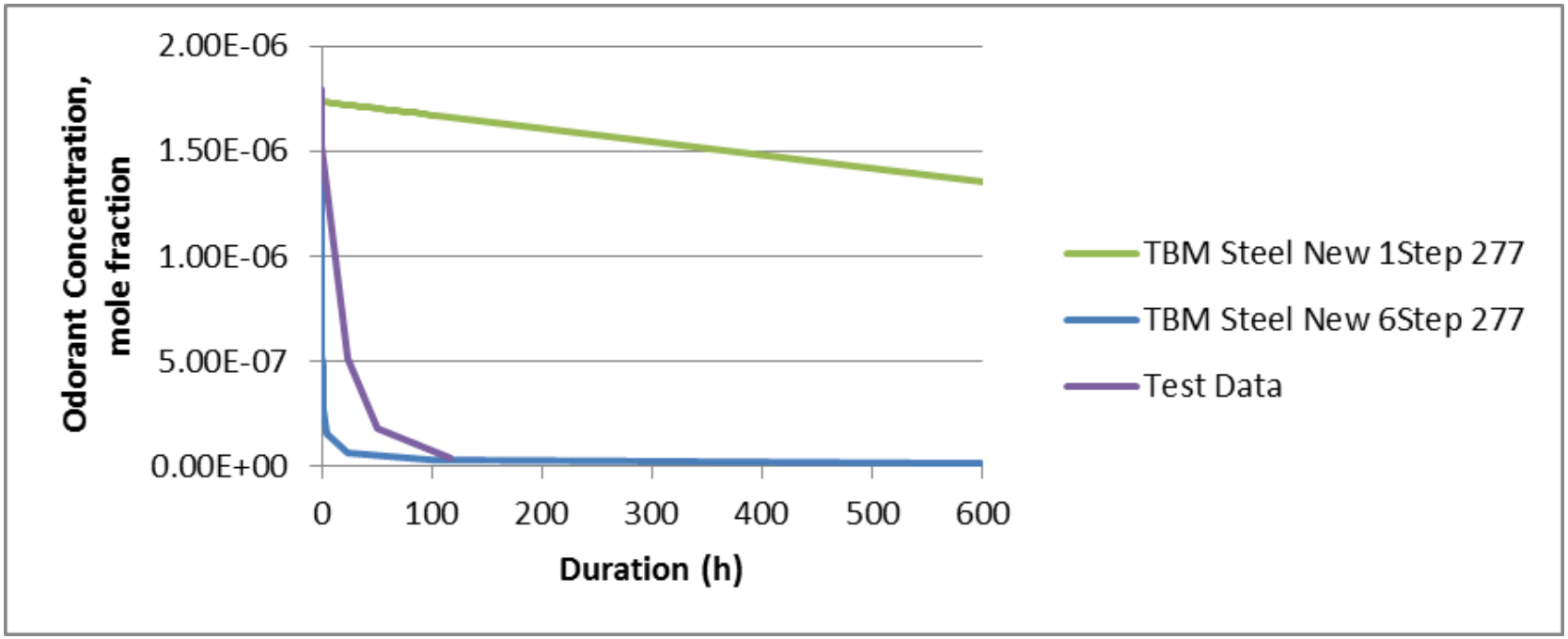
- The third model shifted away from the use of a thin volumetric reaction zone to surface chemistry on the interior wall itself, requiring a shift in both how parameters are treated and which submodels were deployed.
- The multistep process was adsorption followed by reaction on the wall surface.
- Also included was looking at how the presence of small amounts of water impacted the reaction of TBM in bare steel pipe.
- The second order temperature exponent was not required.
- Decent agreement was found with experimental data.

Model Fit in Plastic Pipe



Example of model fit with TBM and THT in plastic pipe

Model Fit in Steel Pipe



Example of model fit with TBM in steel pipe

Overall Model Conclusions

- This project used three iterations of laboratory data to generate the initial models.
- 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.

Collecting Field Data

- One goal of the last 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.

Collecting Field Data

- None of the other project stakeholders wanted to piggy back any pipe onto their existing pipelines.
- GTI's solution was to do odorant analysis during an actual natural gas pipeline installation and/or conditioning project.
- 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.

Project Challenges

- Progress on the final project goal of a user-friendly model was hindered due to lack of field data.
- While the model exists, unfortunately it is in a version that is not easy to use, unless one is familiar with the native software used (Ansys Fluent).

Final Project Conclusions

- 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.

Final Project Conclusions

- 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.

Final Project Conclusions

- The trace constituents water, oxygen, methanol, monoethanolamine (MEA), and hexanes were added to inerted test vessels at concentrations up to the maximum values found in available gas quality 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 (MEA).

Questions?

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> Andy Hammerschmidt, Paul Glanville, Joe Baffoe, Andy Hill, Russell Bora, Dianne Joves, Matthew Donatello, Nicole Reiff, Alan Janos, Nick Daniels, Peter Mulligan, Brian Spillar, Tom Hayes