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Forensic Engineering Investigation of an LP-Gas Installation and an Analysis of Odor Fade

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Gas, Propane, Thermodynamics, Kinetics, Odor Fade

Part 1

Case Study FE Analysis of Odor Fade of an LP-Gas Installation

Abstract

The first part of this presentation is a case study involving a domestic propane gas system, having a buried line between the supply tank and the residence. The gas line was pierced during a landscaping project. This breach was undetected and gas leaked underground; migrating towards the house where it entered under the house. The fugitive gas found a source of ignition, resulting in an explosion and death of the single occupant. Odorant in the gas apparently did not warn the occupant.

In October of 2006, a propane marketer received a phone call from the local fire department to assist in the investigation of an explosion and fire that had occurred the previous evening. The gas company quickly determined that they had filled the tank the previous morning. In assisting the fire department, they found a breach in a buried gas line. A fence post had pierced the line about fifteen feet from the house. A landscaping crew had set the post the previous day.

The sole occupant was killed in the incident. A lawsuit was brought against the landscaper, propane marketer and an ex-employee of the propane marketer. The landscaper quickly settled for their policy limits but the suit against the other two defendants continued for 5½ years. The discovery process yielded the following timeline:

The victim and her husband built the home in 1993. The house was located 2-3 miles from the nearest town or emergency provider and about ½ mile from the nearest neighbor. At that time a gas system

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was installed that included an above ground 500 gallon tank feeding a buried underground polyethylene (PE) line going to the house. A metallic tracer tape was buried alongside the PE line. The pressure was regulated by a first stage regulator at the tank and a second stage regulator at the house[1]. The gas appliances[2] serviced were a boiler, dryer and space heater[3]. In 1996 the gas marketer installed a gas detector with a solenoid valve shut-off ahead of the second stage regulator - as required by state law at the time[4].

The above ground tank was replaced with a buried 1000 gallon tank in 2001. The buried line was modified slightly to accommodate the buried tank and the first stage regulator was replaced[5]. These changes were performed and documented by the same gas marketer[6].

The house was remodeled in the summer of 2005. Sometime before, the area over the buried line was graded to improve drainage[7]. The grading reduced the depth of the buried line from 12-18 inches to about 10 inches in some locations. The remodel included a new detached garage and placing an addition to the house on the original garage footprint. Modifications to the gas system were performed by an ex-employee to the gas provider[8]. The modifications included rerouting of some of the buried PE line and replacement of the second stage regulator. The modifications also, likely, included the removal of the gas detector[9].

The landscaping was modified, in the spring of 2006. The project added numerous plantings; trees, shrubs and the like. In the fall, the single owner[10] had the area fenced to protect the trees from the area's moose and deer. She later decided to remove the fence and have the trees fenced individually.

The day of the incident, the landscaping crew arrived shortly before the propane delivery driver. They had previously removed the encircling fence and had started fencing the individual trees. It was never determined whether the buried line had been breached before the driver completed his delivery; however the landscaping crew worked the rest of the day without detecting a gas leak.

About 7 PM, an explosion occurred and the residence caught on fire. The sole occupant was killed in the initial explosion. Post incident, an analysis of gas taken from the underground tank indicated that the odorant was about 8 times the recommended amount[11].

The best scenario, largely undisputed, is as follows:

- LP-gas was delivered while landscapers were beginning fencing modification.
- The landscapers failed to have someone locate the gas line before driving fence posts for fencing.
- A fence post pierced the buried line (~10" below surface)
- The breach in line undetected due to wet soil (stayed underground)
- Fugitive gas followed gas line to house
- The fugitive gas entered the house through the foundation

- The odorant was 'scrubbed' from the LP-gas – from the breach to the house,
- The fugitive gas found source of ignition
- The ignition resulted in explosion
- The single occupant died on the scene from initial explosion.

Odor fade or 'scrubbing' was not established, however it was not disputed since this is a well-established phenomenon. The issues remaining in dispute for this matter were:

- Should the LP-gas provider be aware of modifications, by others, to the system?
  - The grading that reduced the depth of the buried line
  - The removal of the gas detector
- Was the LP-gas adequately odorized?
  - Is there a better odorant?
- Was there a duty to rebury the line to a minimum depth (12 inches)[12]?

While the particular details of this matter are unique, 'Odor Fade' cases have some common aspects; properly odorized gas comes into contact with a material that promotes the conversion of the odorant to a material that does not have a noticeable smell. These contact materials include; iron oxide, soils, masonry or water (e.g. snow). If this 'odorless' gas is outside the delivery system and accumulates, the eventual ignition can result in substantial property damage, injury or death.

Part 1, above describes an incident where odor fade occurred due to contact with the soil surrounding a buried line. Part 2 describes the phenomenon where odorized gas comes into contact with iron oxide.

Part 2
The Thermodynamics of Odor Fade in Propane and LPG

Abstract

Ethyl Mercaptan (Ethanethiol) is the common odorant used in propane and LPG at the 17 ppm level (Ref: National Fuel Gas Code Handbook, 2ND Ed.(1992), Supplement 3: Fuel Gas Odorization EM at level of 17 ppm). The loss of odorant can result in undetected gas leaks leading to fires and explosion. The application of thermodynamics can identify the chemical reaction causing the odor fading, and can help develop measures to guard against fading. Thermodynamics analysis shows that Ethyl Mercaptan is oxidized in the presence of moisture, and evolves to iron oxide (rust) to Diethyldisulfide that, thus, no longer has an odorizer. The free energy of the Diethyldisulfide forming reaction is -5,303.5 calories/mol at room temperature. The equilibrium constant based on the free energy for the reaction strongly favors the diethyldisulfide formation. Although thermodynamics generally is not well suited for determining the kinetics of a reaction, the Mercaptan fade appears to follow the decay law equation $C_t = C_o e^{-Xt}$ where

C_t is the concentration of Mercaptan present in the propane or LPG at time t days; C_o is the original concentration; X = is a constant that depends on the size and condition of the storage container and is on the order of 0.1; and t is time in days.

Discussion

Thermodynamics in the broadest sense is the study of the relationship between energy and materials. The energy may be in the form of heat, chemical, mechanical, or other forms. The materials may be solids, such as metals, or chemical compounds in the form of liquids or gases. In this paper, thermodynamics is used to determine whether a material is stable or whether a reaction with its environment can occur to change it. If the material is found by thermodynamics to react with its environment, the rate of that reaction is generally not available without further analysis.

The Ethyl Mercaptan (Ethanethiol) odorant is added in small quantities to propane or LPG for the purposes of detecting a leak. If the tank contains some amount of water, the steel tank walls may be rusted. As a result, it is appropriate to use chemical thermodynamic analysis to determine if these materials react with Ethyl Mercaptan.

The free energy of formation in calories per mol at room temperature is shown in Table 1.

Table 1 – FREE ENERGY OF FORMATION

Compound	***Formula***	***Free Energy of Formation***
Ethyl Mercaptan	CH_3CH_2SH	-1,280 calories/mol
Diethyldisulfide	$CH_3CH_2SSCH_2CH_3$	-2,280 calories/mol
Dihydrogen oxide	H_2O	-56,687 calories/mol
Hemitite	Fe_2O_3	-177,400 calories/mol
Magnitite	Fe_3O_4	-243,200 calories/mol

CH_3CH_2SH is the chemical formula for Ethyl Mercaptan. The question is: does the presence of rust (Fe_2O_3) cause Ethyl Mercaptan to oxidize and lose its odor?

CH3CH2SSCH2CH3 is the non-odor oxidation product Diethyldisulfide by the reaction:

$$2CH_3CH_2SH + 3Fe_2O_3 = CH_3CH_2SSCH_2CH_3 + H_2O + 2Fe_3O_4$$

The free energy for the above reaction is -5,303.5 calories/mol of CH_3CH_2SH. The negative sign establishes that this oxidation reaction is thermodynamically possible.

It is a good practice to analyze other reactions to see if there are further reactions of the Diethyldisulfide or alternate competing reactions. In this case cited, it appears that the reaction Fe_2O_3 above is the only acting reaction.

- The equilibrium constant "K" for the oxidation reaction above represents the product activities or concentrations, divided by the reactants activities or concentrations:

$$\mathbf{K = (CH_3CH_2SSCH_2CH_3)(H_2O)(Fe_3O_4)^2/(CH_3CH_2SH)^2(Fe_2O_3)^3}$$

- Since H_2O, Fe_3O_4 and Fe_2O_3 are present at unit activity, their numerical activity value is one and thus, they drop out of the equilibrium equation. Therefore, the equilibrium equation becomes:

$$\mathbf{K = (Diethyldisulfide)/(Ethyl\ Mercaptan)^2}$$

- The equilibrium constant is related to the free energy of the reaction (G_{rxn}) by the equation:

$$\mathbf{G_{rxn} = -RTLnK}$$

where R is the ideal gas constant, (1.987 cal/k.mol), T is the absolute temperature (298 K), and Ln stands for natural log.

By this equation, the equilibrium constant K = 7,760

Thermodynamics does not determine the rate of reaction, but merely if the reaction can occur. However, there is a link between the rate of reaction and whether the reaction can occcur since the equilibrium constant, K, is equal to the ratio of the forward rate constant, divided by the backward rate constant.

Since the reaction involves both a fluid and a solid, the size of the tank, i.e. the surface area and volume, are important considerations. This is a surface controlled reaction, therefore, the corrosion products can be passivated by long term exposure and reaction with Ethyl Mercaptan.

- As an example, examining the rate of Mercaptan fade data taken from a rusted 25-gallon tank shows that the form of the equation is similar to the decay formula for a radio isotope.

The formula is: $\mathbf{C_t = C_o e^{-Xt}}$

where C_t is the concentration of Ethyl Mercaptan at time t, and C_o is the initial concentration.

X is a constant based on a specific tank.

For the 25-gallon tank in question, X = 0.1

For this tank, at t = 7 days, the concentration of Ethyl Mercaptan is $C_t = 0.5C_o$.

For t at 1/5 C_o, an illegal low concentration, t = 16 days.

This example of the use of thermodynamics in analyzing odor fade is a demonstration that thermodynamics is a powerful tool used in corrosion analysis and in other areas to determine the possibility of an undesirable reaction occurring.

References

1. The pressure from the first stage regulator was about 10 psig.
2. The gas appliances and in-house gas lines were installed by others – likely subcontractors to the builder.
3. The 1993 gas system was tested and documented in a GAS CHECK® form by the gas marketer.
4. The gas detector requirement was rescinded shortly after.
5. The regulator replacement was the standard practice for this gas marketer.
6. The documented changes were limited to the exterior as the owner/occupants were not home at the time.
7. The grading was noted in the construction permit for the remodel and was likely done by the victim's husband.
8. This ex-employee had installed and modified the original gas system for the gas provider.
9. By this time the gas detector requirement was rescinded and the owner had experienced at least one nuisance shutdown.
10. The husband had died in a car crash, before the subject incident.
11. The odorant used has a vapor pressure less than that for commercial propane. As a result, odorant tends to accumulate in containers after repeated fillings.
12. The state adopted NFPA 58, *LP-Gas Code* which requires that buried lines have a minimum depth of 12", when installed.