ROBUST CHEMICAL REACTIVITY PROGRAM PREVENTS POTENTIAL TANK EXPLOSION

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A 41.6 m^3 storage tank and connected gauge tank last used to store dimethyl sulfate (DMS), was to be decommissioned and removed. DMS is a highly corrosive, combustible liquid used in methylation and quaternization reactions. Review of available product literature (DuPont, 2002) by the decommissioning team indicated that DMS, when mixed with water, will hydrolyze quickly to methyl sulfuric acid and methanol. A subsequent, much slower reaction will hydrolyze the methyl sulfuric acid to sulfuric acid and additional methanol. The reaction rate is known to increase with temperature. Although the hydrolysis reaction was known to be exothermic, no data on the rate or quantity of heat generation was initially found in the literature. The team therefore commissioned in-house lab analyses to characterize the intended reaction. The resulting data showed that the reaction was moderately exothermic. However, the reaction also produced permanent gases that could lead to tank overpressurization given the right circumstances. Discovery of this hazard prompted the team to develop a means to positively limit the amount of DMS in the tank, leaving only residual amounts of DMS to be hydrolyzed.

INTRODUCTION

A 41.6 m^3 storage tank, rated for 1.7 barg at 500 K, was last used to store dimethyl sulfate (DMS). DMS is a highly corrosive, combustible liquid used in methylation and quaternization reactions. Following construction of a new DMS storage tank, the former tank and associated gauge tank (shown in Figure 1) were to be decommissioned. A decommissioning team was formed to plan the necessary decontamination work prior to removal and disposal of the tank. The available product literature indicated that DMS, when mixed with water, will hydrolyze to methyl sulfuric acid and methanol. The methyl sulfuric acid will then slowly hydrolyze to form sulfuric acid and additional methanol. The reaction rate is known to increase with temperature (DuPont, 2002). The team began to form a plan based on the literature information and the supplier's informal advice that dilute solutions of sodium hydroxide or ammonia be used to decontaminate the storage tank and associated piping. Although the hydrolysis reaction was known to be exothermic, no data on the rate or quantity of heat generation was initially found in the literature.

As can be seen in Figure 1, the tank was not equipped with a bottom outlet, and the submersed transfer pump was thought to rest about 8 cm above the tank bottom. This left the team unsure of how much DMS remained in the tank. Because the tank had no cooling, there was considerable concern about whether ambient cooling would be sufficient to cool the reaction. Unwilling to proceed without additional characterization of the reaction, the team commissioned in-house lab analysis to characterize the intended reaction.
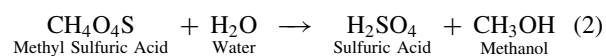
REACTIVITY TESTING

The decommissioning team had decided to use city water to decontaminate the tank, as it was readily available in the plant, an emergency backup supply was available from the plant fire system, and the literature indicated that it would accomplish the decontamination in a reasonable amount of time (DuPont, 2002).

The anticipated initial reaction of DMS with water is:

$$\underset{\text{DMS}}{C_2H_6O_4S} + \underset{\text{Water}}{H_2O} \longrightarrow \underset{\text{Methyl Sulfuric Acid}}{CH_4O_4S} + \underset{\text{Methanol}}{CH_3OH} \quad (1)$$

If given time, a secondary hydrolysis of the methyl sulphuric acid (CH$_4$O$_4$S) will occur as follows:

$$\underset{\text{Methyl Sulfuric Acid}}{CH_4O_4S} + \underset{\text{Water}}{H_2O} \longrightarrow \underset{\text{Sulfuric Acid}}{H_2SO_4} + \underset{\text{Methanol}}{CH_3OH} \quad (2)$$

Each reaction proceeds at a molar ratio of 1:1.

The in-house Advanced Reactive Systems Screening Tool (ARSST$^{\text{TM}}$), shown in Figure 2 was selected to perform the analysis because it would provide both temperature and pressure data as well as rates of temperature and pressure change (Burelbach, 2000). The ARSST functions in an "adiabatic plus" mode, where the sample is heated at a constant rate throughout the entire experiment. Any heating greater than the imposed heating rate is considered to be heat produced by the reaction. The sample is contained in an open 10cc glass vessel, which is placed in a 350cc containment vessel. To ensure that reactants do not boil out of the sample container, at least one test is run at a pressure higher than the lowest boiling reactant or product.

TEST A09291001

6.81 g DMS was charged to the ARSST, padded with nitrogen to about 7 barg, and heated at a rate of 1.13 K/min. When the DMS reached 307°K, 4.88 g city water was charged to the ARSST. For this test, the Pressure/Temperature
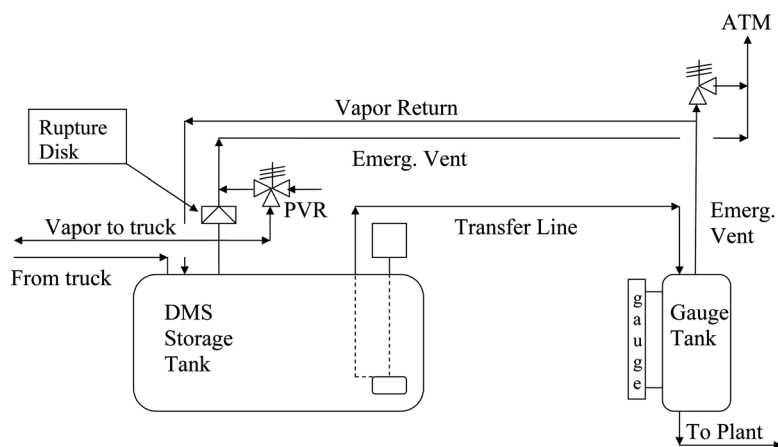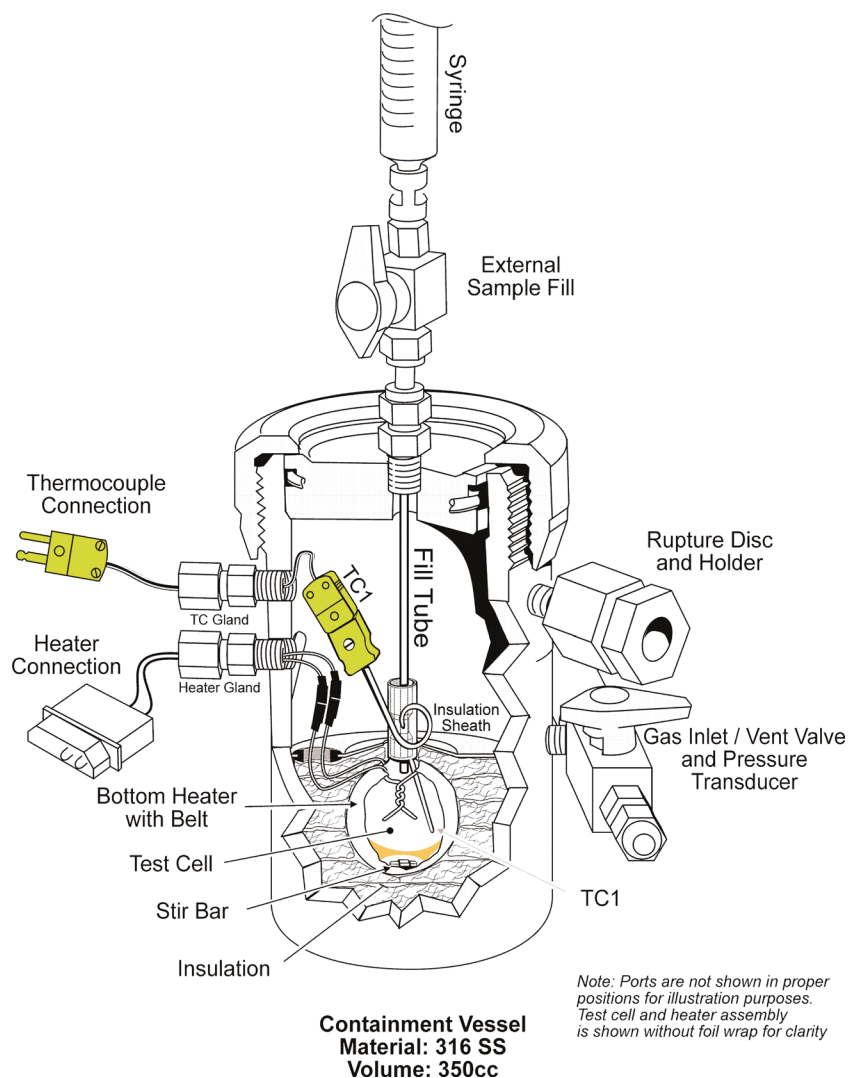
Figure 1. DMS storage and gauge tanks
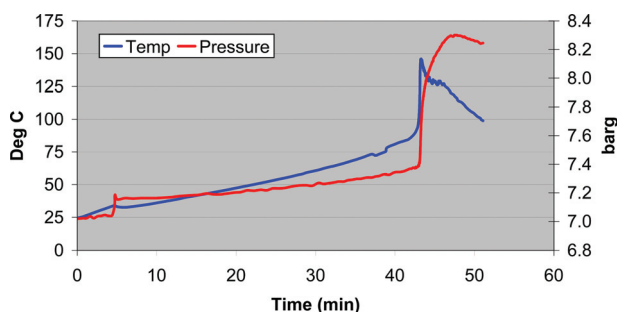
Figure 2. ARSST schematic

Figure 3. Test A09291001 press/temp vs. time

vs. Time and Pressure vs. Temperature charts are shown in Figures 3 and 4, respectively.

The temperature rise ($\Delta T_{\text{measured}}$) for an exothermic event in the ARSST can be calculated in a dynamic test using equation 3 (Theis, 2008):

$$\Delta T_{\text{measured}} = T_{\text{final}} - T_{\text{onset}} - (T_{\text{imposed}})(t_{\text{final}} - t_{\text{onset}}) \quad (3)$$

where $T =$ Temp (K), $t =$ Time (s), and the imposed heating units are K/min, with data taken from the ARSST results.

For this test the measured temperature rise is:

$$\Delta T_{\text{measured}} = 419 - 318 - (1.13 \times (43 - 18) = 72.75 \,\text{K}$$

The reaction onset temperature and duration match well with that in the literature (DuPont, 2002).

The reaction enthalpy can be calculated using equation 4 (Leung, 1986):

$$\Delta H_{RXN} = \frac{\Phi C_p \Delta T_{\text{measured}}}{X} \quad (4)$$

where $\Delta H_{RXN} =$ reaction enthalpy (cal/g), $\Delta T_{\text{measured}} =$ measured temperature rise in the calorimeter, $X =$ mass fraction of limiting reagent (unitless), $C_p =$ Specific heat of the mixture (cal/g °C), $\Phi =$ thermal inertia of test cell (unitless), calculated using equation 5 (Leung, 1986):

$$\Phi = 1 + \frac{m_b C_{p\text{-}b}}{m_r C_{p\text{-}r}} \quad (5)$$

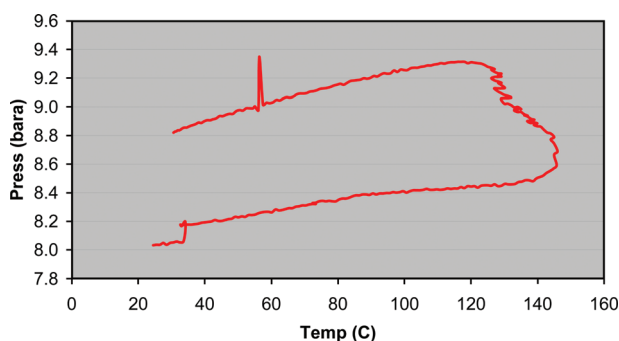where $m_b =$ mass of the test bomb, $C_{p\text{-}b} =$ specific heat

Figure 4. Test A09291002 pressure vs. temperature

of the test bomb material of construction (0.2 cal/g K for glass), $m_r =$ mass of reagents, $C_{p\text{-}r} =$ specific heat of the reagents.

The thermal inertia for this test is:

$$\Phi = 1 + \frac{(1.56 \,\text{g})(0.2 \,\text{cal/g} \cdot \text{K})}{(11.69 \,\text{g})(0.6 \,\text{cal/g} \cdot \text{K})} = 1.04$$

The heat of reaction is then:

$$\Delta H_{RXN} = \frac{(1.04)(0.6 \,\text{cal/g} \cdot \text{K})(72.75 \,\text{K})}{6.81 \,\text{g}_{\text{DMS}}/11.69 \,\text{g}}$$

$$= 77.9 \,\text{cal/g}_{\text{DMS}} = 9,819 \,\text{cal/mol}_{\text{DMS}}$$

Figure 4 shows that the pressure after the reaction cooled to 40°C is significantly higher than the pre-reaction pressure at 40°C. This is indicative of the formation of non-condensable gas (NCG) during the reaction. The amount of gas generated can be determined by subtracting the number of gas moles in the containment vessel prior to the reaction from the number of gas moles following the reaction. Using the Universal Gas Law:

$$\frac{P_1 V_1}{n_1 R T_1} = \frac{P_2 V_2}{n_2 R T_2} \quad (6)$$

where $P =$ absolute pressure (bar), $V =$ volume (litres), $n =$ number gas mols, $R =$ Universal gas constant (8.3145 J/mol · k) and $T =$ temperature (K).

Rearranging equation 6 to solve for n_2:

$$n_2 = n_1 \frac{P_2 V_2 R_2 T_2}{P_1 V_1 R_1 T_1} \quad (7)$$

which simplifies to

$$n_2 = n_1 \frac{P_2 T_2}{P_1 T_1} \quad (8)$$

given that V and R are constant.

Given that 1 mol gas occupies 22.4 liters at 273°K and 1.01 bara (STP), and the ARSST containment vessel volume is 0.350 liters, the number of pre-reaction gas moles (after injecting the water) using equation 8 are:

$$\# \,\text{mol}_i = \frac{273.15}{313.46} \times \frac{8.19}{1.01} \times \frac{0.3501}{22.4 \,\text{l/mol}} = 0.124$$

The post-reaction gas volume is:

$$\# \,\text{mol}_f = \frac{8.89 \,\text{bara}}{8.19 \,\text{bara}} \times 0.124 = 0.135$$

The number of moles of NCG generated is then:

$$\# \,\text{moles generated} = \# \,\text{mol}_f - \# \,\text{mol}_i$$

$$= 0.135 - 0.124$$

$$= 0.011 \,\text{moles generated.}$$

On a mol/kg_{DMS} basis:

$$\frac{0.011 \text{ moles}}{0.00681 \text{ kg}_{DMS}} = 1.62 \text{ mol/kg}_{DMS}$$

It was later discovered that the heat of DMS hydrolysis in water has been reported to be 21,110 cal/mol (21.11 kcal/mol) (Robertson, 1966). ΔT_{ad} may be determined from this information using equation 9:

$$\Delta T_{ad} = \frac{(\Delta H_{RXN})(n)}{\Sigma(m \cdot C_p)_{\text{reagents involved}}} \tag{9}$$

where n = # moles, m = mass and C_p = heat capacity of the reactants.

The expected temperature can be calculated using equation 9 as:

$$\Delta T_{ad} = \frac{(21110 \text{ cal/mol}_{DMS})(\text{mol}_{DMS}(6.81 \text{ g}/126 \text{ g})}{(6.81_{(\text{mass DMS})} \cdot 0.31_{(C_p(\text{cal/g·K}))}}$$
$$+ 4.88_{(\text{mass of water})} \cdot 1_{(C_p(\text{cal/g·K}))})$$
$$= 163 \text{ K}$$

$$\Delta T_{\text{measured}} = \frac{\Delta T_{ad}}{\Phi} = \frac{163}{1.04} = 157 \text{ K}$$

(DMS heat capacity obtained from DuPont, 2002)

Clearly this temperature rise was not seen in the ARSST test carried out. Potential reasons for this include:

- Incomplete hydrolysis of the DMS
- The boiling of methanol (Vapour pressure = 12 barg @ 423°K) consuming the energy that would otherwise raise the reaction mass temperature.
- A reaction other than that predicted above, which also produces the NCG.

Given the boiling point of methanol, it is likely that at least some of the expected heat not observed was used to boil methanol.

POTENTIAL REACTION CONSEQUENCES

The Decontamination Team was concerned that the 25 psig storage tank, with no means of cooling, would not withstand the described reaction. The team posed the following questions:

1. What final temperature and pressure would be expected in a closed tank?
2. If emergency venting were necessary, what vent area would be required?

To answer the team's first question (What final temperature and pressure would be expected in a closed tank should the gas-producing reaction occur?), requires two separate analyses. The first is determining the final temperature should the reaction occur. It has been shown previously in this paper that $\Delta T_{ad} = \Delta T_{\text{measured}} \cdot \Phi =$ approximately 76 K.

This assumes, however, that the same ratio of DMS: water is used. The reaction can produce 78 kcal/kg DMS. The team believes that the amount of DMS currently in the tank is between 300 and 3,000 kg. The final temperature of this reaction, accounting for the thermal inertia of any water added, can be expressed as:

$$T_{\text{final}} = T_{\text{initial}}$$
$$+ \frac{(\Delta H_{rxn})(\text{kg DMS})}{[(\text{wt frac} \cdot \text{DMS})(C_{p\text{-DMS}}) + (\text{wt frac H}_2\text{O})(C_{p\text{-H}_2\text{O}})]}$$
$$\times (\text{kg DMS} + \text{kg H}_2\text{O}) \tag{10}$$

This simplifies to:

$$T_{\text{final}} = T_{\text{initial}} + \frac{78X}{1 - 0.69X} \tag{11}$$

where X = the Mass fraction of DMS in the mixture.

Figure 5 shows a plot of ΔT vs. DMS mass fraction.

To determine the final pressure, one must know the starting pressure, # final and initial moles in the vapour space, initial and final temperature, initial volume (with only DMS in the vessel) and final volume (with DMS + water in the vessel). This information would allow us to solve for final pressure using equation 12:

$$P_f = P_i \times \frac{T_2}{T_1} \times \frac{n_2}{n_1} \times \frac{V_2}{V_1} \tag{12}$$

Expressed in terms of M, the starting mass of DMS (kg), and the amount of water added (expressed in terms of X, the mass fraction of DMS, and M), and assuming a starting temperature of 323 K, the final pressure can be expressed as:

$$P_f = (1.01) \times \left[1 + \frac{78X}{(323 - 222.9X)}\right] \times \left[\frac{1857 + 1.59M}{1857 - 0.034M}\right]$$
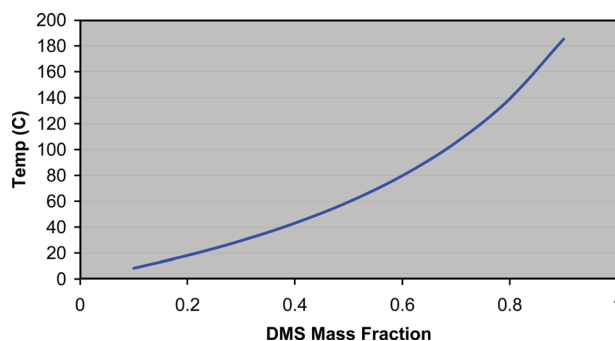$$\times \left[\frac{41640 - .757M}{41640 - 1.757M - \left(\frac{M}{X}\right)}\right] \tag{13}$$
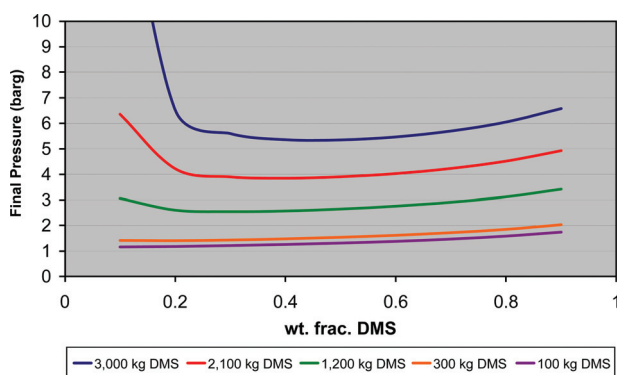
Figure 5. Temp. rise vs. DMS mass fraction

Figure 6. Final pressure vs. DMS wt. fraction

Figure 7. dT/dt vs. $-1000/T$

Figure 6 shows P_{final} vs. mass fraction of DMS for selected quantities of DMS between 100 and 3000 kg. One can see from the chart that while increasing quantities of water results in decreasing final pressures, the resultant decrease in tank void volume eventually offsets the gains of additional water, causing the final pressure to increase. This is of importance to the decommissioning team as they plan to fill the tank and recirculate it through the gauge tank.

The second question asked by the team is whether emergency venting will be necessary, and if so what vent area would be required. Because the mass of DMS in the tank is unknown, we must assume the worst case. Figure 6 shows that 3,000 kg of DMS produces the highest final pressure. For vent sizing, it was assumed that the tank contained 3,000 kg DMS, and that the final DMS mass fraction would be 0.4 (i.e., 7,500 kg of water would be added, resulting in the tank being about 25% full).

The vent area required to safely vent this reaction can be calculated (Theis, 2008) as:

$$A_v = \left\{ \frac{3.5E-3}{14.5P\left[1+\frac{1.98E3}{14.5P^{1.75}}\right]^{0.286}} \right\} \left[\frac{(\dot{T}+14.5\dot{P})V}{C_D} \right] \quad (14)$$

where A_v = vent area (m^2), P = relief set pressure (barg), $\dot{T}$ = rate of temperature rise at relief setpoint (C/min), $\dot{P}$ = rate of pressure rise at relief setpoint (psi/min), V = volume of reactants (m^3) and C_D = discharge coefficient of the relief device.

As stated, $\dot{T}$ must be determined at the mixture's boiling point at the relief set pressure. To determine this a second ARSST test (A09291002) was conducted near the relief setpoint of 10 psig. Because equation 14 determines reaction energy input to the system from dT/dt at the relief set point, we must determine from the high-pressure test (A09291001) what value dT/dt is at the boiling point in the low pressure test. dT/dt vs. $-1000/T$ for both tests is plotted in Figure 7. From this chart, we can see that the low pressure reaction tempers at about 113°C, which
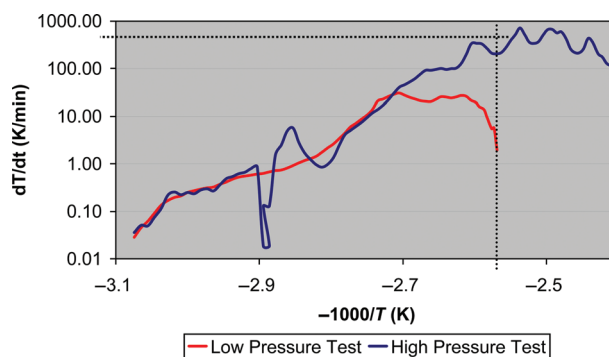
corresponds in the high pressure test to dT/dt = 205 K/min. The gas generation is taken as the highest dP/dt observed over the test period. From the ARSST data, this was determined to be 1.86 bar/min.

Using equation 14, and assuming a 10 psig relief set point, we have:

$$A_v = \left\{ \frac{3.5E-3}{(14.5)(0.69)\left[1+\frac{1.98E3}{(14.5\times0.69)^{1.75}}\right]^{0.286}} \right\}$$

$$\times \left[\frac{(205+(14.5\times4.2))9.722}{0.97} \right] = 0.33\,\text{m}^2$$

This is equivalent to a vent diameter of 0.64 m.

DISCUSSION AND DECONTAMINATION PLAN

The published reaction enthalpy is larger than that measured in the ARSST by a factor of more than 2. This might be explained by the boiling of methanol, or due to a secondary reaction producing the permanent gas. Knowing the potential temperature and pressure rises predicted for neutralization of the largest predicted quantity of DMS, the team decided on a strategy to positively minimize the inventory of DMS. It was also decided at this point to forgo further testing in a more sensitive instrument, such as a Vent Sizing Package (VSP) or Accelerating Rate Calorimeter (ARC). While either of these instruments would provide more precision and detail about the reactions, such information was not required to implement the planned actions. It was decided to forgo any attempt to identify the permanent gas as well.

Because the tank had been in service for so long, the team was unsure if it may have settled unevenly, or if sludge of any type may have accumulated in the tank. Either of these could prevent the DMS from draining to the pump end of the tank. A plan was devised to remove all piping and the submersible pump, which is mounted on an 18″ nozzle, from the tank. The tank end opposite the pump

would then be lifted several inches to ensure the remaining DMS drains to the pump end. A diaphragm pump equipped with a suction wand would then be inserted through the 18″ nozzle to remove as much DMS as possible. The team felt this would ensure no more than 100 kg DMS would be left in the tank. Water (50°C) would then be introduced through the open nozzle, which would provide adequate venting if necessary.

Using $\Delta H_{rxn} = 21.110 \text{ kcal/mol}_{DMS}$, the maximum adiabatic temperature rise for a mass ratio of 1.4:1 DMS to water (as in the above tests) would be as shown above.

Using $1.62 \text{ mol}_{NCG}/\text{kg}_{DMS}$, the maximum volume of gas generation would be:

$$V_{NCG} = \frac{1.62 \text{ mol}_{NCG}}{\text{kg}_{DMS}} \times 100 \text{ kg}_{DMS} \times \frac{22.4 \text{ l}}{\text{mol}} \times \frac{\text{m}^3}{1{,}000 \text{ l}} = 3.6 \text{ m}^3$$

As can be seen in Figure 6, if the vessel were closed, the final pressure would be assured to be less than the tank rating of 1.7 psig.

CONCLUSION

The initial plan for decontaminating the DMS tank was to fill the tank with water, ensuring that all surfaces of the tank were in contact with the solution. Although available literature suggested this was an acceptable approach, the team was not satisfied with the limited thermodynamic information about the reaction. Rather than proceed using the limited information available to them, the team required additional testing to obtain the missing information.

It was the team's diligent search for answers that uncovered a potentially devastating incident which, under the correct circumstances, could have caused an explosion and catastrophic loss of containment of a particularly hazardous substance

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