# **Effect of Temperature on Failure of Gas Cylinders**

M. Nasrul Haque and E. Haque

A number of ammonia cylinders burst during open storage in a field in the month of June. The cause of failure was studied. No flaws in the cylinder material were detected. Under normal conditions, the tangential stress  $(5.4 \text{ kg/mm}^2)$  in the cylinder is well below the yield strength  $(49 \text{ kg/mm}^2)$ . The tangential stress increases with the rise of temperature of the ammonia. As long as some vapor exists inside the cylinder, the liquid remains in equilibrium with the vapor, the cylinder pressure is equal to the vapor pressure of ammonia at that temperature, and the rise in tangential stress is insignificant  $(0.14 \text{ kg/mm}^2)^{\circ}$ C). However, as the temperature increases, the specific volume of the liquid ammonia inside the cylinder also increases. The cylinder is completely filled with liquid under certain conditions in accordance with the bulk thermal expansion of the liquid; under these conditions, the cylinder pressure rises sharply with increased temperature, causing a large rise in tangential stress  $(4.76 \text{ kg/mm}^2)^{\circ}$ C). Thus, an approximate 10 °C temperature rise in a cylinder filled with liquid ammonia can lead to failure.

Keywords ammonia cylinder, liquid, pressure, rupture, tangential stress, temperature, vapor

# 1. Introduction

A NUMBER of ammonia cylinders ruptured during the month of June while being stored in an open field. This study investigated the failures to determine their cause. Each cylinder could accommodate 95 L of anhydrous ammonia liquid and was intended to hold about 50 kg of ammonia—an amount that would leave 12.38 L of vapor volume at ambient temperature (25 °C). Reportedly, one of the failed cylinders that was examined had been filled with 52 kg of ammonia. The cylinders were designed for a service pressure of 0.18 kg/mm<sup>2</sup> and were tested at a hydraulic pressure of 0.50 kg/mm<sup>2</sup>. Each cylinder had an internal diameter of 350 mm and a nominal wall thickness of 5.8 mm. The minimum yield point and the minimum tensile strength of the cylinder material as per specification were 30 and 45 kg/mm<sup>2</sup>, respectively.



Fig. 1 Crack along the side of the weld

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# 2. Investigation and Tests

### 2.1 Physical Inspection

The rupture in each case occurred along the side of the welded joint of the cylinder (Fig. 1). The rupture had a fish-mouth appearance with a thick lip (Fig. 2).

## 2.2 Tensile Testing

Tensile specimens were prepared from material taken across the weld joint so that the weld was in the middle of each specimen. An ultimate tensile strength (UTS) of 60 kg/mm<sup>2</sup> and a yield strength of 49 kg/mm<sup>2</sup> were obtained. The resulting stress-strain diagram is shown in Fig. 3.

### 2.3 Chemical Analysis

The cylinder material was found to contain 0.09% C, 0.05% Si, 0.81% Mn, 0.037% S, and 0.025% P.

### 2.4 Metallographic Study

Figure 4 shows the crack as observed on the cross section of the cylinder wall. The arrow indicates the crack initiation point. The tensile specimens were treated to reveal the weld section



Fig. 2 Fish-mouth appearance of the rupture

and the grain flow of the parent metal (Fig. 5). Figure 6 shows the lamellar structure of the plate used for cylinder construction. The white phase represents the proeutectoid ferrite, and the dark phase is pearlite.

The structural changes at the welded joint are shown in Fig. 7. Figure 7(a) reveals the coarse structure of the heat-affected zone. This structure is of the Widmanstätten type, with lines of ferrite (white phase) breaking up the pearlite areas (dark phase). This nonequilibrium structure is common in a low-carbon steel in which transformation occurs from large austenite grains during a moderately fast rate of cooling. Figure 7(b) shows the deposited metal consisting of columnar ferrite (white phase) and pearlite (dark phase).

## 3. Discussion

It is apparent that the crack initiated somewhere near the weld joint and proceeded along its length (Fig. 1, 2, and 4). However, macroscopic and microscopic examination revealed no significant flaw in the weld. Also, during tensile testing the specimens failed through the weld metal (which was in the middle portion of each specimen) at a reasonably high tensile stress



Fig. 3 Stress-strain diagram of cylinder material



Fig. 4 Crack initiation at the point of contact between the filler metal and the base metal

(60 kg/mm<sup>2</sup>). Therefore, failure was not caused by welding defects. Figure 1, however, shows that cracks initiated on both sides of the weld bead, as there had been a notch effect due to weld-metal deposit. The bottom crack propagated ahead of the top crack, causing failure in this particular instance.

The ammonia inside a cylinder with a filled in-service pressure of 0.18 kg/mm<sup>2</sup> produces a tangential stress of  $\sigma = 5.4$  kg/mm<sup>2</sup> on the cylinder wall, given by:

$$\sigma = \frac{PD}{2t}$$

where *P* is the cylinder pressure, *D* is the inside diameter of the cylinder, and *t* is the thickness. The cylinder was tested with a hydraulic pressure of  $0.50 \text{ kg/mm}^2$ , which is well above the service pressure, but the tangential tensile stress so developed was only 15 kg/mm<sup>2</sup>. Based on the tensile test results, the cylinder is expected to fail at a tangential stress of about 60 kg/mm<sup>2</sup>, which, ignoring any notch effect, is significantly above the normal tangential stress of 5.4 kg/mm<sup>2</sup> and even greater than the stress of 15 kg/mm<sup>2</sup> developed during hydraulic testing. How-



Fig. 5 Tensile specimen after rupture. Necking and rupture in the weld region are visible, as is the grain flow in the parent metal.



Fig. 6 Lamellar structure of the plate used for cylinder construction



Fig. 7 Photomicrographs of the weld joint. (a) Heat-affected zone. (b) Deposited zone



Fig. 8 Change in vapor pressure of ammonia with temperature. Source: Ref 1

ever, as the temperature rises, the pressure inside the cylinder will also increase, leading to a higher tangential stress.

Vapor pressure increases with increasing temperature. Figure 8 shows the change in vapor pressure of ammonia with temperature (Ref 1). In a closed system having both vapor and liquid, vapor will be in equilibrium at each temperature with the liquid. The pressure of the container will be the vapor pressure, as shown in Fig. 8. When the vapor is in equilibrium with the liquid in a closed vessel, the specific volume of the saturated vapor,  $V_{sv}$ , decreases with temperature (Fig. 9), and the specific volume of liquid,  $V_{sl}$ , increases (Fig. 10) (Ref 2).

In a closed system, the total mass of ammonia will remain constant at any temperature. If the volume of the cylinder is Vand the volumes of liquid and vapor are  $V_1$  and  $V_v$ , respectively, then at any temperature:



Fig. 9 Relationship between specific volume of saturated ammonia vapor and temperature for a closed container. Source: Ref 2

That is,

$$\frac{V_1}{V_{\rm sl}} + \frac{V_{\rm v}}{V_{\rm sv}} = m \tag{Eq 1a}$$

$$V_1 + V_v = V \tag{Eq 1b}$$

where *m* is the total mass of ammonia.  $V_{sl}$  and  $V_{sv}$  can be determined from Fig. 9 and 10, respectively. If *m* and *V* are known,  $V_1$  and  $V_v$  can be calculated from Eq 1(a) and 1(b).

Figure 11 shows the change in  $V_1$  and  $V_v$  with the rise in temperature in a cylinder with a volume of 95 L. No vapor will remain in the cylinder when it contains 52, 50, or 48 kg of ammonia at temperatures of about 58, 70, or 81 °C, respectively. Above these temperatures, the cylinder will contain only liquid, provided that the expansion of the steel cylinder is neg-



Fig. 10 Relationship between specific volume of liquid ammonia and temperature. Source: Ref 2

ligible. The average volume coefficient of thermal expansion,  $\beta$ , for a given liquid from temperature  $T_1$  to  $T_2$  can be obtained from the following relationship (Ref 3):

$$\beta = \frac{\left(1 + \frac{T_2 - T_1}{T_c - T_2 - 6}\right)^{0.3} - 1}{(T_2 - T_1)}$$

where  $T_c$  is the critical temperature of the liquid, which is 405.43 K for ammonia. The average value of  $\beta$  can be obtained as  $3.80 \times 10^{-3}$  m/m  $\cdot$  °C for a change in temperature from 25 to 58 °C. Since the linear coefficient of thermal expansion,  $\alpha$ , is equal to  $(\frac{1}{3})\beta$ , the average value of  $\alpha$  for liquid ammonia in the above temperature range would be  $1.27 \times 10^{-3}$  m/m  $\cdot$  °C. This value of  $\alpha$  is much greater than that of carbon steel  $(1.17 \times 10^{-5} \text{ m/m} \cdot ^{\circ}\text{C})$ . Thus, the expansion of the cylinder volume can be ignored. When the cylinder contains only liquid, an increase in temperature will attempt to increase the volume of liquid, but since the volume is fixed, the liquid pressure will instead rise very sharply. The pressure of compressed liquid, *P*, can be obtained from the following relationship (Ref 4):

$$V = V_{\rm sl} \left[ 1 - c \ln \left( \frac{\beta + P}{\beta + P_{\rm vp}} \right) \right]$$
(Eq 2a)

where V is the volume of the compressed liquid, and  $V_{sl}$  is the specific volume of the liquid at the vapor pressure,  $P_{vp}$  (in bars). The value of  $P_{vp}$  for each temperature can be obtained from Fig. 8. Values for c and  $\beta$  are obtained from:

$$c = j + k\omega_{SRK}$$
 (Eq 2b)

$$\beta = P_c [-1 + a(1 - T_r)^{1/3} + b(1 - T_r)^{2/3} + d(1 - T_r) + e(1 - T_r)^{4/3}]$$
(Eq 2c)



Fig. 11 Change in volume of liquid and volume of vapor with temperature in a cylinder with a volume of 95 L

where

$$e = \exp(f + g\omega_{SRK} + h\omega_{SRK}^2)$$
 (Eq 2d)

and

$$T_{\rm r} = \frac{T}{T_{\rm c}}$$

where

T = temperature (in K)  $T_{c} = \text{critical temperature (in K)}$  $P_{c} = \text{critical pressure (in bar; 113.5 bar for ammonia)}$ 

 $\omega_{SRK}$  = acentric factor (0.262 for ammonia) (Ref 5)

The values of the constants (Ref 4) for Eq 2(b) to 2(d) are: a = -9.070217, b = 62.45326, d = -135.1102, f = 4.79594, g = 0.250047, h = 1.14188, j = 0.0861488, and k = 0.0344483.

The value of  $V_{sl}$  can be obtained either from Fig. 10 or from the following correlation (Ref 6):

$$\frac{V_{\rm sl}}{V^*} = V_{\rm R}^{(\rm o)} \, (1 - \omega_{\rm SRK} \, V_{\rm R}^{(\delta)}) \tag{Eq 3a}$$

where  $V_{\rm R}^{(0)}$  and  $V_{\rm R}^{(\delta)}$  are state function and deviation function, respectively, and are given by:

$$V_{\rm R}^{(0)} = 1 + a(1 - T_{\rm r})^{1/3} + b(1 - T_{\rm r})^{2/3} + c(1 - T_{\rm r}) + d(1 - T_{\rm r})^{4/3} \quad 0.25 < T_{\rm r} < 0.95$$
 (Eq 3b)

$$V_{\rm R}^{(\delta)} = \frac{\left[e + fT_{\rm r} + gT_{\rm r}^2 + hT_{\rm r}^3\right]}{T_{\rm r} - 1.00001} \qquad 0.25 < T_{\rm r} < 1.0 \quad ({\rm Eq} \, 3{\rm c})$$

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V\* is a pure component characteristic volume (in liter/mol) generally within 1 to 4% of the critical volume, which is 0.0701 L/mol for ammonia (Ref 5). The values of the constants in Eq 3(b) and 3(c) are: a = -1.52816, b = 1.43907, c = -0.81446, d = 0.190454, e = -0.296123, f = 0.386914, g = -0.0427258, and h = -0.0480645.

Figure 12 shows the effect of temperature on cylinder pressure for 52 kg of ammonia. Up to about 58 °C, the cylinder pressure is only the vapor pressure and follows the line AB. As mentioned before, at 58 °C the cylinder is filled only with liquid. Above this temperature, the cylinder pressure, P, that will result with increased temperature can be obtained from Eq 2(a), which will follow the line BC in Fig. 12. When the cylinder pressure reaches a point such that the tangential stress is equal to the UTS of the cylinder material, the cylinder will fail. Point C in Fig. 12 shows that a temperature of 69 °C and a corresponding cylinder pressure of 2 kg/mm<sup>2</sup> are required to produce failure of a cylinder with an internal diameter of 350 mm, a wall thickness of 5.8 mm, and a UTS of 60 kg/mm<sup>2</sup>.

A rough idea of the cylinder temperature that could be reached in direct sun can be obtained from the energy balance:

That is,

$$\alpha_{\rm s}q = \varepsilon\sigma(T^4 - T_{\infty}^4) + h(T - T_{\infty}) \tag{Eq 4}$$

where  $\alpha_s$  is solar absorptivity (which is 0.75 for light gray oil paint); *q* is solar heat flux (in W/m<sup>2</sup>, which is about 900 W/m<sup>2</sup> at noon during summer in Bangladesh) (Ref 7);  $\varepsilon$  is emissivity (which is 0.9 for light gray oil paint);  $\sigma$  is the Stefan-Boltzmann constant (in W/m<sup>2</sup> · K<sup>4</sup>, which is 5.669 × 10<sup>-8</sup> W/m<sup>2</sup> · K<sup>4</sup>); *T* is the equilibrium temperature of the surface (in K);  $T_{\infty}$  is the surrounding temperature (in K, which is about 313 K at noon during summer in Bangladesh); and *h* is the convective heat-transfer coefficient (in W/m<sup>2</sup> · K).

Using these data in Eq 4, the equilibrium temperature of a flat surface exposed to direct sun is 92 °C. Although the temperature of a cylinder would be slightly different from this value, it might easily reach 69 °C if the cylinder was exposed to direct sun for a long time.



Fig. 12 Effect of temperature on cylinder pressure for 52 kg of ammonia

#### 4. Conclusions

The cylinders failed due to an unusual rise in tangential stress when the containers became completely filled with liquid as a result of a rise in temperature, presumably due to extended exposure to the summer sun.

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